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PRACTICAL CHEMISTRY

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PRACTICAL CHEMISTRY

FOR

INTERMEDIATE CLASSES

BY

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PREFACE

This book has been written in response to many requests from my fellow teachers and from the students who attend my lectures and demonstrations. The exercises represent a two years' course of Practical Chemistry which was specially drawn up for my pupils reading in the Intermediate Science Classes at the Khalsa College, Amritsar.

Each demonstration describes the class work for a period lasting 1½ to 1¾ hours, but teachers can sub-divide demonstrations according to the time at their disposal, the capability of the students, and the resources of the laboratory. There is no objection, in many cases, to two students working together, *e.g.*, this may be done with advantage in, say, Demonstrations III to XXXV, but in all cases tests and experiments on analysis should be performed by each individual student.

All the experiments described have been successfully performed by large classes of elementary students and are therefore thoroughly reliable.

The practical classes should be arranged so that the subject of study is understood by the students before they enter the laboratory. The amount of work to be got through in each of these demonstrations is large and can only be done properly when :

(1) The arrangements in the laboratory are such that everything necessary for the performance of the experiments is ready for the student when he asks for it.

(2) The student is a conscientious worker.

(3) The theory of the experiment and general hints on manipulation have been given some time previously in the lecture room.

(4) The student is given at least one day's notice of the practical

work which he will be required to do when the class next meets, so that he is able to study the details of the experiments at leisure.

If the student knows the subject of his experimental work beforehand this book will enable him to read up, in conjunction with his lectures, all that he will be required to do. It is hoped that, in cases where difficulties are likely to arise, adequate explanation of the theory of the experiments has been given to make the subject clear. The order of treatment is that observed in the course of lectures which I give in conjunction with these demonstrations.

I trust that the manner of presentation of the section on Volumetric Analysis will help the beginner to overcome the difficulties which are often encountered when commencing this important branch of Practical Chemistry.

At the conclusion of many of the demonstrations will be found certain experiments headed "Demonstrations." These experiments are either somewhat complicated or involve the use of apparatus which cannot be issued to the whole class. The full explanation of these experiments is not given in the text. It is intended that the demonstrator should perform the experiments during the practical lesson before sections of ten to sixteen students and at the same time give details of the theory of the experiments.

The students should be encouraged to ask questions, to examine and draw sketches of the apparatus used and to write in their notebooks a brief account of the method employed.

I wish to express my sincerest thanks to Prof. B. H. Wilsdon, of Government College, Lahore, for the interest he has taken in this book. He has most kindly read through the sheets before they went to Press and has offered many valuable suggestions which I have been most grateful to accept for the improvement of the work.

I wish also to express my thanks to my sister who passed the proofs through the Press.

H. B. DUNNICLIFF.

SIMLA,
September, 1916.

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A copy of this list of rules should be pasted in the cover of the note-book of every student in the laboratory.

RULES FOR THE GUIDANCE OF STUDENTS WORKING IN THE CHEMICAL LABORATORY.

This note-book is NOT TO BE TAKEN AWAY from the Chemical Laboratory.

Write only in black pencil or black ink and use the right hand page only.

Commence the account of a new experiment on a fresh page

At the head of the page write clearly the date and then, in a larger hand, the title of the experiment you are about to describe.

Write legibly *on the lines of the book* and make a point of being neat both in your work and in your books.

Leave a clear line between the title and the description of the experiment.

Do not cramp your work.

Do not use odd scraps of paper for noting down data. Put your data straight into your book.

Give, *in the first person,* a clear and concise account of the method you employ and write down what you do, etc , *at the time* you perform the experiment.

Describe and carefully draw sectional diagrams of the apparatus you use.

Never use a word of which you do not know the meaning.

Imagine that you are describing something which has to be read *and understood* by someone who has no knowledge of the subject. In this way you will learn to use simple words and your attempts to be clear will help you to understand your work better in addition to giving you a command of grammatical English.

" Rough " working may be done *neatly* on the left hand page.

After using a bottle return it to its place on the shelf.

Do not remove from the demonstration table apparatus or reagents supplied for the use of the whole class. Take sufficient material for your purpose and perform your experiments at your bench.

Report all breakages *at once.* Use *small* quantities.

You are liable to be marked "absent" for (1) lateness, (2) insufficient or untidy work, (3) not following out the instructions given to you by the Professor or Demonstrator.

Students may be called on to pay partial or full cost of apparatus broken by them through carelessness or disobedience.

I have read and understood the above rules.

*Signed*______________________________

PART I

GENERAL INORGANIC CHEMISTRY AND SIMPLE QUALITATIVE ANALYSIS

RULES FOR THE GUIDANCE OF STUDENTS IN WRITING UP LABORATORY NOTES

Write only in black pencil or black ink and use the right hand page only.

Commence the account of a new experiment on a fresh page.

At the head of the page write clearly the date and then, in a larger hand, the title of the experiment you are about to describe.

Write legibly *on the lines of the book* and make a point of being neat both in your work and in your books.

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PART I

DEMONSTRATION 1

A STUDY OF THE BURNERS USED IN THE LABORATORY

Draw diagrams of your apparatus.

Write down what you do and see at once.

If you do not understand anything, ask the demonstrator.

When chemical action takes place between gases with the evolution of light and heat a " flame " is produced.

An " inflammable " substance is any substance which will burn.

In this exercise you will study what happens when gases burn under various conditions.

The lowest temperature at which a gas or a mixture of gases will begin to burn is called the " ignition temperature " or " ignition point " of that gas or mixture. Each inflammable substance has its own " ignition point."

EXPT. 1.—**Temperature of Ignition or Ignition Point.**—Pour a few drops of carbon disulphide into a small porcelain capsule. Heat a little strong sulphuric acid in a test-tube. Place the hot end of the test-tube near the porcelain capsule. If the temperature of sulphuric acid is greater than 150° C. the carbon disulphide will catch fire. The reason is as follows:—

The vapour of carbon disulphide and air make an inflammable mixture. The temperature of air is below the ignition point of the mixture. The temperature of the hot sulphuric acid is above the ignition point of the mixture and so the mixture catches fire.

Note that sulphuric acid has nothing to do with the experiment except that it can be heated above 150° C. Try the same experiment with a glass rod heated in the flame.

The inflammable material continues to burn because its own combustion provides sufficient heat to keep the temperature near the inflammable material above the "ignition point."

If the flame is cooled below the ignition point it will go out, *vide* Expt. 3, page 6.

Expt. 2.—**The "batswing" or "fishtail" burner.**—Light the gas as it issues from the batswing burner. Note that the ignition point is too high for it to be set on fire by the hot glass rod. You must use a burning match. This burner is designed primarily to give light.

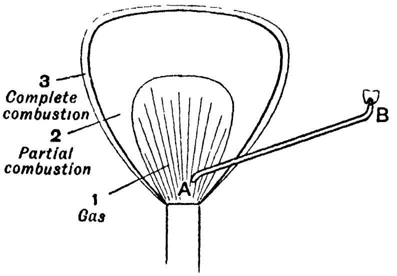


Fig. 1.

Draw a sketch of the flame and notice how the jet is made. The flame consists of three parts.

(1) A blue inner portion. This consists of unburnt gases. This can be shown by putting the end *A* of the bent glass tube in the blue part of the flame. The gases pass up the tube and will burn as they come out of the end *B*.

If the gas does not burn readily, vary the angle at which you hold the tube *AB*.

(2) The portion which is luminous. The combustion here is not complete. Depress a piece of cold porcelain in the flame and describe what you see. The black deposit is unburnt carbon. By interfering with the flame this carbon has been unable to reach the outermost zone.

(3) In which complete combustion is taking place. Look carefully for this very pale blue zone. It is the hottest of the three.

Put a piece of iron wire in each of the three portions of the flame and notice what happens in each case.

The luminosity of the middle portion of the flame is increased by the heat imparted to it by the hot outer mantle.

EXPT. 3.—**The Bunsen burner.**—Examine the Bunsen burner carefully. Take it to pieces. Notice:

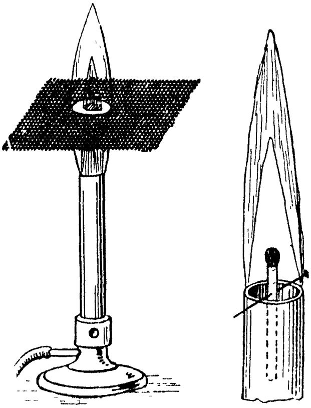
(1) The tiny orifice from which the gas issues.
(2) The tube with holes at its base.
(3) The mechanism for closing those holes.

Fit the burner together and connect it to the gas supply. Close the holes, turn on the tap and light the gas.

Examine the flame carefully as described in Expt. 2 and notice that, though different in shape, it really possesses the same parts as the batswing (fishtail) flame you studied just now.

Open the holes slowly and carefully observe what happens. The luminosity gradually disappears and the flame becomes pale blue and transparent. The flame may run down the tube and set the gas on fire at the narrow orifice inside the tube. This is called " striking back."

Adjust the holes so that the flame is quite clear and steady. Depress a piece of gauze into it, holding the gauze horizontally. Notice the ring of red-hot iron surrounding the comparatively cold inner zone.



FIGS. 2 and 3.

Try to draw off and ignite unburnt gases from the inner zone with your bent tube.

Turn the gas off. Stick a pin through a match one-third its length from its head and hang it inside the burner as shown in Fig. 3. Light the gas. The match does not catch fire. Why? Lower the gas. As soon as the inner tip of the outer zone comes into contact with the match-head, the match catches fire.

Depress porcelain into the clear flame and note that there is no soot deposited. There is no " zone of partial combustion."

Turn off the gas. Hold a piece of wire-gauze about 1½ to 2 inches above the burner. Apply a match to the gas *above the* *gauze.* The gas catches fire but does not burn below the gauze. The reason is that the material of which the gauze is made, being a conductor of heat, conducts the heat away and the temperature below the gauze is lower than the " temperature of ignition " of the gases. It is upon this principle that the Davy Safety Lamp is made.

Air is necessary for the combustion of the gas you are using. In the case of the batswing (fishtail) flame all the air used comes from *outside* the burner. The Bunsen burner is so constructed that air can mix with the gas *before* it commences to burn. That is what the holes at the base are for.

You are provided with some material which will burn slowly and give smoke (smoulder). Light your Bunsen burner and open the holes. Put the smouldering material near the air-holes and you will see the smoke sucked in. It will give you an idea of how the air is sucked in by the gas as it comes out of its narrow orifice and mixes with the gas as it passes up the tube.

If you have too little air your flame will be smoky. If you have your air correctly adjusted your flame will be clear and colourless.

If you have too much air the flame first burns irregularly and then " strikes back."

N.B.—If when the air-holes are full open the flame is still luminous or smoky, hand it back to the laboratory assistant. The remedy is to take the burner to pieces and partially close up the gas orifice, but the student is not to attempt to do that, as he has not the proper tools and may ruin the burner.

EXPT. 4.—**The mouth blow-pipe.**—Draw a sketch of a blow-pipe.

Close the air-holes at the base of the Bunsen burner and make a small luminous flame for use with the blow-pipe.

To maintain a continuous blast of air through the blow-pipe a certain amount of practice is required. To obtain this continuous blast use the contraction of your cheeks to expel the air from your mouth on to the blow-pipe. Breathe through your nose and keep the cheeks more or less distended. You cannot expect to be able to use a blow-pipe perfectly at the first attempt. It requires patience and perseverance. Do not try to blow hard. A gentle blast is sufficient. Do not direct the blast *down* the tube, but

DEMONSTRATION 2

To make a Wash-bottle

Expt. 5.—**To cut a glass tube or rod.**—The method given here applies to tubes or rods of narrow diameter. The demonstrator will show how tubes of wide diameter are cut.

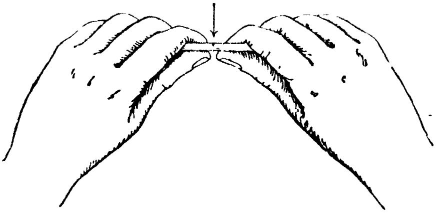


Fig 5.

Do not waste material. Cut off as much glass as you are likely to require.

Lay the glass tubing on the table and hold it firmly in the left hand. With a triangular file make a single scratch across the tube at the place where the tube is to be cut.

Take the tube in both hands as shown in Fig. 5 and arrange that the scratch is on the side of the tube opposite to that on which the thumbs are. The thumbs should be on either side of the scratch. Now pull the tube as if you wanted to stretch it, and at the same time bend it outwards by means of the thumbs.

The glass should break with a straight edge. If it does not break it is because the file was wrongly used. Make a second scratch at the same place as the first was made and try to break the tube again.

The cut edge is rough but if it is held in the hot, clear Bunsen flame the edges melt and become quite smooth.

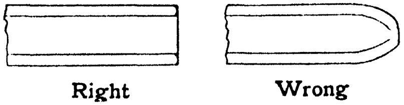


Fig. 6.

Be careful not to overheat a tube when rounding off the edges or the tube will collapse as shown in the figure (Fig. 6).

ALWAYS ROUND OFF the edges of a cut rod or tube in this way before pushing the rod or tube into or through a cork or a piece of rubber tubing The rough edges cut the cork, etc.

EXPT. 6.—**To bend a glass tube.**—For bending the tubes required to make a wash-bottle a batswing flame is used. Never use the ordinary Bunsen flame. Hold the tube in the length of the flame so that 2 to 3 inches are being heated. When heating the tube it must be constantly rotated backwards and forwards about a horizontal axis.

Two bent tubes are necessary, one bent once at an angle of 135° (Fig. 7 (1)), and one bent at an angle of 45° (Fig. 7 (2)).

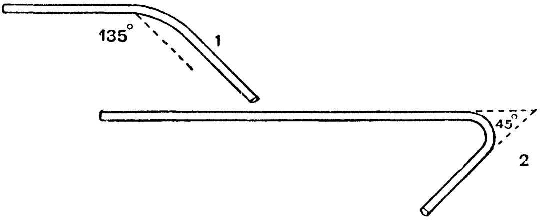
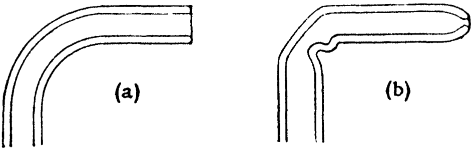


FIG. 7.

At first the student will find it difficult to get a good bend as shown in Fig. 7, as not only is it hard to obtain a long, sweeping curve, but there is a tendency for the tube to collapse and buckle if not properly heated, *vide* Fig. 8 (*a*) and (*b*).



Right. Wrong.

FIG. 8.

A long bend as shown in Fig. 7 (2) is made by bending the tube progressively. First warm it between points *A* and *B* (Fig. 9). As the bend starts at *C*, warm the tube to the right of *C* and the bending will go on between *C* and *B*, and so on until the actual sweep of the bend occupies about 2 inches of the length of the tube, but the bend will be quite uniform. It is possible to get the bend in one operation, but the beginner will find it difficult. The tube must be rotated while it is being heated. As far as possible allow the heated tube to bend by its own weight.

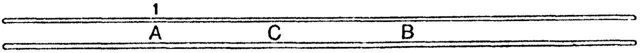


Fig. 9.

If the whole curve does not lie in one plane warm the bend and, while warm, press it flat on a sheet of asbestos boarding.

Expt. 7.—**To draw out a jet.**—Heat a piece of tubing in a clear Bunsen flame until it thickens at the place where it is heated.

The tube will look like Fig. 10. Take the tube out of the flame and pull it *slowly*. It will then assume the shape shown in Fig. 11.

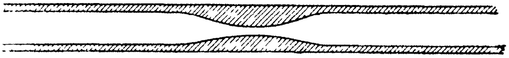


Fig. 10.

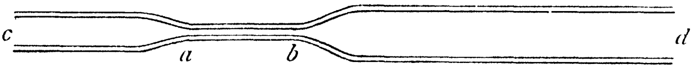


Fig. 11.

Notice that the glass between *a* and *b* is nearly as thick as that at *ca* or *bd*.

Draw a file once across the middle of the constricted portion and break the tube into two pieces. You now have two jets. Round off the ends *c* and *d*.

The narrow orifice of the jet may be rounded off by very carefully putting it in the hot portion at the base of the Bunsen flame. (See Fig. 22, page 18.) Be very careful not to seal the narrow orifice altogether.

Expt. 8.—**To make a capillary tube.**—Proceed as in Expt. 7. When the tube has thickened, pull the two ends apart rather more quickly and a long, thin-walled tube, called a "capillary tube," will be formed. This is required in the next demonstration.

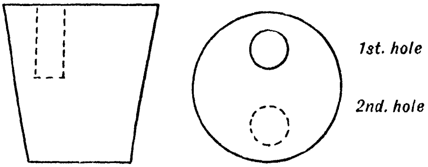
It is possible that, when heating glass tubes either for the purpose of bending them or making jets or capillaries, the tube may lose its transparency at the point where it is being heated.

The loss of transparency is called "devitrification" and is due either to overheating or to the glass being old.

EXPT. 9.—**To bore a cork with two holes which will accommodate the two tubes bent in Expt. 6.**—Select a cork of which the narrow end just goes with difficulty into the neck of the flask to be used to make your wash-bottle. Wrap the cork in paper and soften it by rolling it on the floor under the sole of your boot. It will be found that the cork can now be pushed into the neck of the flask quite easily, and that it will make a good, tight fit.

Choose a cork-borer the external diameter of which is just a shade smaller than the external diameter of the glass tubing for which you are about to bore the hole.

Hold the cork on the table with the left hand. Dip the cork-borer in a 50 per cent. solution of glycerine in water and place the cork-borer on the cork to one side of it.



FIGS. 12 and 13.

Be sure you are holding the borer vertically. Press downwards and twist the hand first 180° to the right and then to the left until the borer has passed about half-way through the cork. Pull the borer out again. If it seems to be tight it will be easily withdrawn if given a slight twisting motion.

The cork is now turned upside down, and by an eye estimation the point where the borer should have come out is marked.

Hold the cork firmly. Dip the borer into the glycerine and bore again at the marked point. The borer should come out at the same point as that at which the boring commenced, and a clean straight hole will be the result.

Bore the second hole in exactly the same manner. The two holes should be exactly parallel. Push the piece of cork out of the borer by means of the iron rod provided with the set of borers.

EXPT. 10.—**To fit the wash-bottle together.**—Be sure that the ends of your bent tubes are rounded off. Wet the two tubes and push them through the two holes in the cork. Fit the jet on to the tube with the 45° bend and the apparatus should look like Fig. 14 (*a* and *b*).

See that the borings, etc., are air-tight by putting water all round the two borings and also round where the cork is fitted into the neck of the flask. Close the jet end *A* with your finger and blow at the mouth-piece end *B*. If no bubbles appear where the water is applied the apparatus is air-tight.

The apparatus should be so arranged that the neck of the flask can be held in the right hand and the flexible jet worked simultaneously with the index or second finger (Figs. 14*c* and 32, page 33). Arrange your tubes so that *A B* is a straight line.

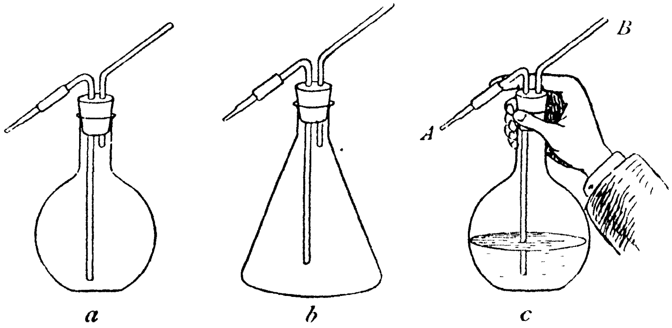


FIG 14.

EXPT. 11.—**To insulate the neck of the wash-bottle against heat.**—A wash-bottle has frequently to be used with hot water. In order to make it possible to handle the bottle when hot a flask of the form shown in Fig. 14*a* is used and thick string is wound round the neck to make a layer of insulation against the heat.

The method of winding the string is shown in the diagrams (Figs. 15 and 16). Lay one free end of the string along the neck of the flask and hold it with the thumb of the left hand. Now wind the string round the neck of the flask and at the same time bind down the free end of the string which has been laid along the neck. This is shown diagrammatically in Fig. 15.

The windings must be tight and so bound that each successive turn touches the previous one.

When the winding has gone to within an inch of the mouth of the flask, pull tight the free end of the string which has been bound to the neck of the flask and cut it off sharp and short.

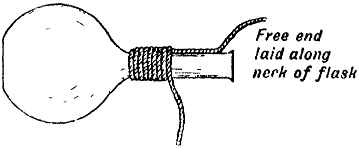


FIG. 15.

Now lay a loop of thin string along the neck of the flask with the loop at the mouth of the flask and then continue binding the thick string round the neck of the flask, passing it over the loop string. When the windings have reached the mouth of the flask, the appearance will be as shown in Fig. 16.

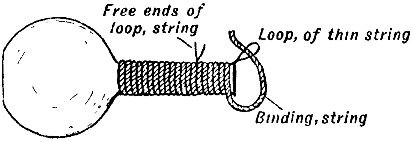


FIG. 16.

Now pass the free end of the thick binding string through the loop and, holding the binding with the left hand, pull the free ends of the loop string. It will pull the free end of the binding string back through the binding. Pull it tight. The loop will pass right through. Cut off the free end of the binding string and the binding is complete.

DEMONSTRATIONS

How to cut a wide tube.

1st Method.—With string.—Take the tube and wind two rolls of paper round it, leaving a small space between the two rolls (Fig. 17). One man holds the paper rolls at *A* and *B*. A second man winds a piece of coarse string twice round the tube between the paper rolls. The first man holds the paper firmly and the second pulls the ends of the string backwards and forwards, keeping the string tight round the glass tube. The glass gets very hot. Without pulling the string away, pour cold water on the glass between *A* and *B*. The tube breaks. Wide bottles may be cut into halves in this way.

2nd Method.—Make a file-mark all round the tube and then lay wetted blotting-paper round the tube on each side of the file-mark.

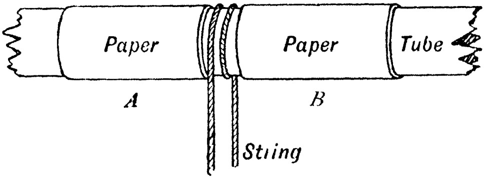


FIG. 17.

Heat the tube at the file-mark with a fine blow-pipe flame. The tube will split across.

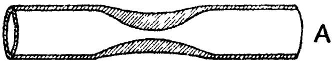
3rd Method.—Make a file-mark round the tube and touch the file-mark with a small red-hot point of glass. The tube will crack along the file-mark and spread all round the tube. If the crack does not pass all round the tube, again touch the end of the crack with a red-hot point of glass and the crack will spread round the tube.

How to Seal a Wide Tube.

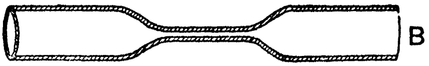
Use a foot blow-pipe. *During all heating rotate the tube.*

1. At the point at which it is desired to seal it heat the tube in a smoky blow-pipe flame.

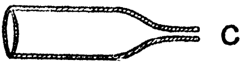
2. When the tube has become heated turn on the blast and heat the tube till it thickens Fig. 18 (*A*).



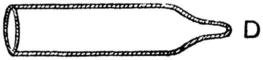
3. Draw it out slowly (*B*).



4. Cut the narrow portion midway (*C*).



5. Seal off the end of constricted part (*D*).



6. Heat the cone-shaped end, with constant blowing at the open end of the tube. The tube will first assume the shape *E* and later on will become like *F*.

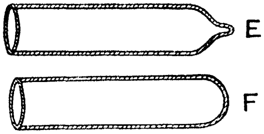


FIG. 18 (A to F).

7. Put the rounded end in the smoky flame and then allow it to cool slowly.

The demonstrator will show and explain the use of:

([illegible]) An air-bath.
([illegible]) A water-bath.
([illegible]) A sulphuric-acid-bath.
([illegible]) A paraffin-bath.
([illegible]) A thermostat and regulator.

DEMONSTRATION 3

MEASUREMENT OF THE BOILING POINT. DISTILLATION

EXPT. 12.—**Determination of the boiling point of a liquid. Distillation.**—A "distillation" flask is a round-bottomed flask with a long neck into which is sealed a glass tube of narrow bore.

Fit the neck of the flask with a cork. Soften the cork by rolling it and bore a hole through it which will take the thermometer provided. (Expt. 9, page 11.)

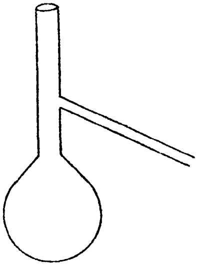


FIG. 19.

Pass the thermometer through the cork until, when the cork is fitted in the neck of the flask, the bulk of the thermometer is opposite the position of the insertion of the tube in the neck of the flask. Select a cork which fits the neck of the condenser tube and bore a hole in it which will accommodate the side (delivery) tube of the flask. Pass the delivery tube right through the cork as shown in the diagram (Fig. 20). In this way the distillate cannot come into contact with the cork.

Put some glass beads in the flask to avoid "bumping." Now pour some of the given liquid into the flask, taking care to hold the flask slantwise so that the side tube points upwards. This prevents any of the liquid from running down the side tube.

Fit up the apparatus shown (Fig. 20). Note that cold water from the tap enters the lower end of the condenser. Light the burner and heat the flask until the temperature indicated by the thermometer is constant. This temperature is "boiling point."

You are to heat your flask on wire-gauze or on a sand-bath, but this is not absolutely necessary.

The demonstrator will show you the distillation of a liquid that boils at nearly 200° C. The flask will be heated by a naked luminous flame.

The liquid which collects in the receiver is called the "distillate."

Write an account of what you have done and draw a diagram of your apparatus.

If the liquid has a low boiling point (say) below 80° C., a water-bath is used.

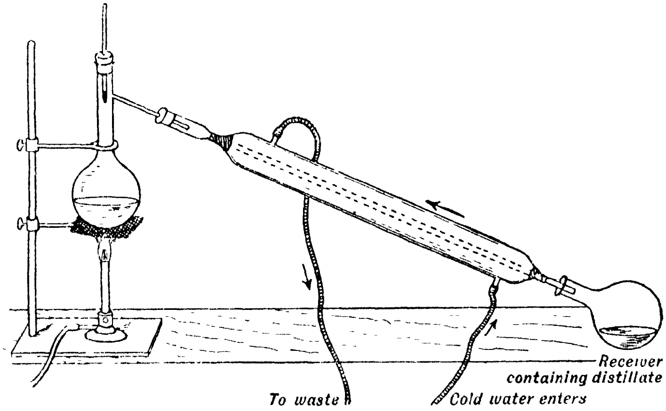


Fig 20.

If the distillate is inflammable the end of the condenser should be passed through a cork fitted in the neck of a distillation flask. The side tube of this distillation flask should be fitted with a long piece of rubber tubing and the free end of the rubber tubing should be put down a sink-hole or in a draught (fume) closet.

Expt. 13.—(i) **To make a capillary tube.** (ii) **To determine the melting point of a given solid.**—Make a capillary tube as explained fully in Demonstration 2, Expt. 8, page 10.

To fill the tube: Melt a little of the substance in a small porcelain capsule. Then lay the capillary tube so that it is practically horizontal and dips in the liquid (Fig. 21). The molten substance will flow up the tube. If the substance solidifies before sufficient has entered the tube, melt what is already in the tube by holding it *near* the Bunsen flame and let it run out. Now *warm* the tube before allowing the molten substance to run into it.

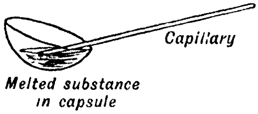


FIG. 21.

Seal off the end of the capillary tube by holding one end in the hot region at the base of the Bunsen flame, as shown in Fig. 22 Fasten the capillary to the thermometer by a rubber band. (To make a rubber band cut a piece one-eighth inch long off an ordinary piece of narrow bore rubber tubing.)

The ring should be so arranged that it is *above* the surface of the liquid which is being used to heat the substance (Fig 23). Use a suitable bath depending upon the melting point of the substance. Water, glycerine and sulphuric acid baths are most usual.

Fit the thermometer into a cork along the side of which is cut a V-shaped groove, and fit this cork into the neck of a long-necked bolt-head flask.

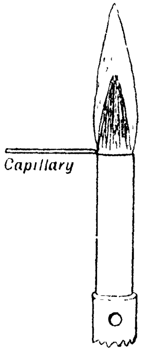


FIG. 22.

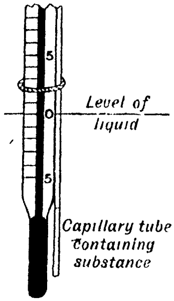


FIG. 23.

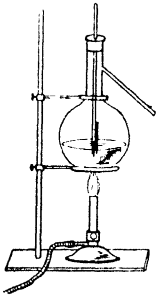


FIG. 24

A 100 c.c. distillation flask suits admirably. Fasten the flask in a stand by a padded clamp and heat slowly with a small flame (Fig. 24). Notice the temperature when the substance in the capillary tube ceases to be opaque. Write down the temperature *in your note-book, not on a loose scrap of paper.*

Remove the burner and notice when the opacity in the capillary tube reappears.

Observe the temperature and *write it down in your note-book, not on a loose scrap of paper.*

The readings should be about the same. If they are not exactly or nearly the same it is not the fault of the substance; *you* have probably made some mistake. Make a new clean capillary and try again.

Pure substances have sharp melting points. You are given a pure substance.

N.B.—If there is a slight and constant difference in the two readings it is probable that the first reading (melting point) is more exact because it is more easy for a liquid to be supercooled and therefore its solidification to be suspended than for a solid to be superheated and have its melting point delayed.

DEMONSTRATIONS

(Draw diagrams of the apparatus in your note-books.)

(1) Distillation under reduced pressure. The action of a suction pump will be demonstrated and explained.

(2) Reflux condenser.

(3) Air condenser for heavy boiling point substances.

(4) Distillation in steam.

(5) Dry distillation (*vide* also Demonstration 15, "Carbon").

Rules to be observed when using Chemical Balances

1. See that the adjustment of the balance is correct before you start weighing.

If the balance is out of order report the matter to the demonstrator, who will have it attended to.

2. Never put chemicals directly on the pan of the balance. Chemicals should be weighed on a watch-glass or in a weighing bottle.

3. Do not put anything on to or remove anything from the pans of the balance while the balance is swinging.

4. Raise or lower the beam by turning the handle for the purpose with the left hand.

5. Weights must never be touched with the fingers. Forceps are provided for the purpose.

There are only two proper places for the weights: (1) in their correct places in the weight-box; (2) on the pan of the balance.

6. The object to be weighed is always placed on the left-hand pan of the balance, the weights on the right-hand pan.

7. Never weigh a hot vessel.

8. If you lose a weight, or if any weights are missing from your box, report the matter at once to the demonstrator.

DEMONSTRATION 4

USE OF THE PIPETTE AND BURETTE

EXPT. 14.—**The pipette.**—Draw a sketch of a pipette. Note the scratch on the stem. The instrument is filled by putting the drawn-off end into the liquid and sucking the other end till the liquid rises above the scratch. Remove the instrument from the mouth and quickly put the index (first) finger, previously moistened, over the hole, as shown in Fig. 25.

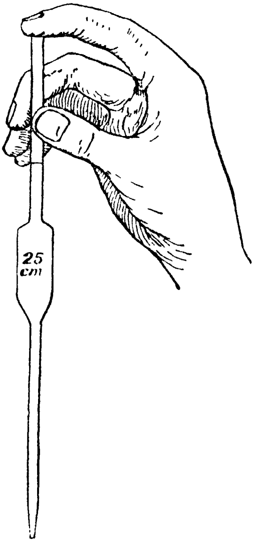


FIG. 25.

By raising the finger slightly, liquid will drop from the pipette till the plane of the scratch when held at the level of the eye makes a tangent with the round portion of the meniscus (Fig. 26). To allow the pipette to deliver the liquid inside it place the open end in the vessel which is to receive the liquid, and lift the finger from the mouth-piece of the pipette. Allow the liquid to flow slowly from the pipette. After the liquid has ceased to flow from the pipette touch the surface of the liquid with the tip of the pipette. You will notice that there is a drop of liquid left in the instrument; **do not blow that drop out.** The pipette is made **to deliver** the volume of liquid engraved on its bulb.

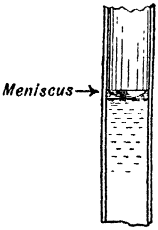


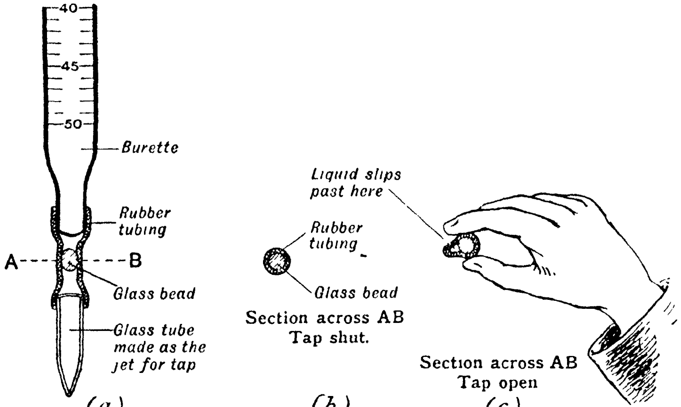
FIG. 26.

Fill and empty a pipette several times to get used to manipulating it.

EXPT. 15.—**The burette.**—Draw a sketch of the burette supplied to you. Note whether it has (1) a glass tap, (2) a rubber and glass tap regulated by a metal pinch cock, or (3) a "bead" tap.

The bead tap is a very cheap and efficient form of tap. It is made as follows:

Draw off a glass jet, as described in Demonstration 2, round the edges and connect it to the end of a burette tube by a rubber connection. Procure a glass rod which is just a tight fit for the rubber tube, and cut off a piece about three-tenths inch long. Round off the edges. It will now look like this . Wet it and slip it into the rubber tube till it is half-way along the length of the rubber tube. Now slip the free end on to open end of the burette. Fig. 27(*a*) represents a sectional diagram of the tap.



(*a*)

Section across AB
Tap shut.
(*b*)

Section across AB
Tap open
(*c*)

FIG. 27.

To use the tap: Pinch the rubber connecting tube where the bead is and pinch a little on the far side of the centre. The rubber will bulge and the liquid slips past the bulge. With a little practice perfect control can be obtained (Fig. 27(*c*)).

Note the following points in using these instruments:

1. Before using the burette or pipette always wash them with the liquid for which they have to be used.

2. Put the burette in a stand. Clamp it firmly but not so tightly as to break the glass. See that it is vertical and not so high that you are unable to place your eye at the same level as any gradation on the burette to which you are likely to want to fill the burette.

3. **There is absolutely no need to fill the burette to the zero mark.** All volumes may be estimated by difference.

4. Put a funnel in the mouth of the burette and pour the liquid in carefully. Remove the funnel before using the burette.

5. If the outside of the burette becomes wetted see that it is dried.

6. See that your tap (1) does not leak, (2) contains no air-bubbles. The two kinds of flexible tap can most easily be cleared from air-bubbles by turning the tap upwards and opening it quickly. The air is then driven out by the flow of liquid.

EXPT. 16.—**Find the volume of the gas in the given cylinder.**—You are given a small gas cylinder partly filled with gas and partly with water, and standing inverted in a small "gas tray" containing water (Fig 28). Take a gummed label and stick it to the outside of the glass so that one edge is at same height as the height of the liquid. Now take the cylinder out of the gas tray. Fill up the cylinder with water with a pipette, taking careful note of how many times you empty the pipette into the cylinder. You will probably overrun the label; if so, carefully withdraw one pipetteful of the liquid from the cylinder, and add water to the cylinder up to the mark from the burette.

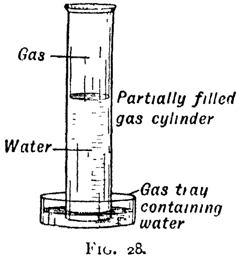


FIG. 28.

Repeat the measurement several times.

Tabulate your results.

Reading No	Capacity of pipette	No of times full pipette was run into cylinder	Readings on burette to make up difference			Capacity.
			at beginning	at end	volume	
1	50 c c	5	2·1 c c	7·4 c c	5·3 c c	250 + 5·3 = 255·3 c c.
2	50 c c	5	7·4 c c	12·8 c c	5·4 c c	250 + 5·4 = 255·4 c c
3	30 c c	8	12·8 c.c.	28·0 c c	15·2 c c	240 + 15·2 = 255·2 c c.

Average = 255·3 c.c.

Required volume of gas was 255·3 c.c. *Ans.*

Expt. 17.—**To find the diameter of a single shot.**—Take a test-tube on a stand and mark a definite height upon it by sticking a label on the outside of it.

Find the volume (x c.c.) of the tube up to the height of the label by the method described above (Expt. 16). Now put some shot into the tube to any height which is distinctly below the height of the label. Run in water again and find out how much has now to be added to fill the tube up to the label (y c.c.).

Describe exactly all that you do. Tabulate your results thus:—

Volume of tube taken = x c.c.

Volume of water required to fill the tube up to mark after inserting shot = y c.c.

∴ Volume of the shot = $(x - y)$ c.c.

Count the shot put into the tube. Number of shot used = z.

∴ Volume of a single shot = $\left(\frac{x-y}{z}\right)$ c.c.

The volume of a sphere is $\frac{4}{3}\pi r^3$.

Where $\pi=\frac{22}{7}$ and r=the radius of the sphere and $r=\frac{\text{diameter}}{2}$.

$\therefore$ Required volume of a single shot $=\frac{4}{3}\pi\left(\frac{\text{diameter}}{2}\right)^3$.

$$i.e.\ \frac{4}{3}\pi\frac{(\text{diameter})^3}{8}=\frac{x-y}{z}.$$

$$\therefore\ \text{Diameter}=\left(\frac{6}{\pi}\cdot\frac{(x-y)}{z}\right)^{\frac{1}{3}}\text{cm.}\quad \textit{Ans.}$$

These results should be obtained with the help of the four-figure Logarithm tables at the end of the book (pages 272 and 273).

General Hints

1. Always replace a bottle in its proper place immediately after use.

2. Replace stoppers in bottles to which they belong. If you have flat-stoppered bottles take the stopper from the bottle with the back of the first and second fingers and hold the bottle with the same hand. See Fig. 29.

When you replace the bottle on the shelf it will come naturally to you to replace the stopper at once.

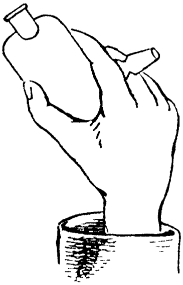


Fig. 29.

3. Keep your bench clean and tidy.

4. Enter your observations, weighings, etc., in your note-book immediately you make them. Never use "scrap paper" or trust to memory.

5. Remove solids from bottles by means of a small, clean spatula. Do not use the same spatula for two different substances without cleaning the spatula.

6. Write your results in tabular form where possible. Draw diagrams to illustrate your reports on experiments.

7. Do not remove from the demonstration table apparatus or reagents supplied for the use of the whole class. Take sufficient material for your purpose and perform your experiments at your bench.

Report all breakages *at once.*

Use small quantities.

DEMONSTRATION 5

STUDY OF PHYSICAL AND CHEMICAL PROPERTIES

Write down each observation at once.

EXPT. 18.—**Physical properties of substances. Action of heat on given substances.**—Describe the given substances as minutely as you can.

Note any peculiarities in shape.

Describe fully what happens when each is heated.

Is any gas or vapour evolved ?

Does anything condense on the upper part of the tube ?

What is the residue like ?

EXPT. 19.—**Deliquescence.**—Expose some of the given substance *A* to the atmosphere and observe all that happens. Notice that it gets moist and finally becomes liquid.

The substance has dissolved in the water which it has taken out of the atmosphere.

The substance *A* is said to be "deliquescent."

EXPT. 20.—**Crystallisation.**—Put some zinc in dilute sulphuric acid. Set aside until the action ceases. Filter, evaporate down and set aside. Notice that a solid separates in small pieces, each possessing a definite geometrical shape. These small pieces are called "crystals," and the process is called "crystallisation."

When a substance owes its geometrical shape (*i.e.* its crystalline form) to the presence of one or more molecules of water, this water is called "water of crystallisation." Sometimes the water of crystallisation gives a definite colour to the substance.

Expt. 21.—**Water of crystallisation** (*a*).—Examine *B*. Notice that it is blue and crystalline. Take a little in a test-tube and heat it. Drops of liquid (water) condense on the upper part of the tube. On heating it loses " water of crystallisation " and falls to a powder. The powder is white. Allow the tube to cool. Now pour a few drops of water on the powder. It recovers its blue colour because the " anhydrous " salt combines with water to form once more the crystalline body (copper sulphate crystals).

(*b*).—Heat some of the pink substance, *C*. It turns blue. Drop water on the blue substance. It recovers its pink colour (crystals of cobalt chloride).

Expt. 22.—**Efflorescence.**—Expose some of the substance *D* to the atmosphere. Notice that it loses its geometrical shape and falls to a powder. This is due to the crystals losing water. The substance *D* is said to be " efflorescent."

Expt. 23.—**Intumescence.**—Heat *E* (1) in a test-tube, (2) on a wire. Notice how it swells up, water, etc., are given off. This process of swelling up on heating is called " intumescence."

Expt. 24.—**All crystalline substances do not contain water.**—Heat *F* and observe that the substance melts but that no water is given off. (*Cf.* also substance *H*.)

Expt. 25.—**Decrepitation.**—Heat *G* in a test-tube. Notice the sharp crackling noises which are emitted. This is called " decrepitation."

Expt. 26.—**Sublimation.**—Heat some of the crystals of *H* in a test-tube. Observe that the substance *does not melt*, but that it is converted into vapour and that the vapour condenses on the upper part of the tube as a *white solid*. When a solid is converted into the condition of vapour without passing through the liquid state it is said to "sublime." The process is called " sublimation." Test the vapour with red and blue litmus papers. The gas will appear to be first alkaline and then acid. Two gases are present, one, the alkaline gas, is less " dense " (heavy) than the other (the acid one), so it passes up the tube more quickly.

EXPT. 27.—**Gaseous diffusion.**—The process by which gases spread themselves through other gases is called "gaseous diffusion." A very heavy gas will "diffuse into" or mix with a lighter gas.

The cylinder *K* contains a very heavy gas—it is brown in colour, so you can see it. The cylinder *L* contains air. The brown gas is about 5½ times as heavy as air. Invert the cylinder of air over the cylinder of brown gas. Let them stand in a safe place so that they will not get knocked over. After a short time you will find that the two cylinders look equally brown, showing that the heavy gas has diffused upwards and mixed with the air.

EXPT. 28.—**Adsorption.**—Take one of these two cylinders containing brown gas and in it put a piece of ordinary wood charcoal. Slip on a cover-glass and let the cylinder stand. In a few minutes the colour will disappear from the cylinder. The charcoal has condensed the brown gas over its surface and in its pores. This process is called "adsorption." *This process is a physical and not a chemical one.* If you heat the charcoal in a test-tube it will again part with the brown gas.

EXPT. 29.—**Description of elements.**—You are given specimens of various elements. Describe their appearance and physical properties.

Heat each of them in contact with air and write down all you observe.

Take careful note of the two elements which are liquids at ordinary temperatures.

One is a metal ....mercury.
One is a non-metal ......bromine.

Notes to Demonstrators

Expt. 18.—Any substances, crystalline or amorphous, may be given. Substances of which the large crystals are easily obtained are common salt (rock salt), alum, and copper sulphate.

Expt. 19.—*A*, Fused calcium chloride or caustic soda.

Expt. 21*a*.—*B* is $CuSO_4,5H_2O$.

Expt. 21*b*.—*C* is $CoCl_2,6H_2O$.

Expt. 22.—*D*. Crystals of washing soda ($Na_2CO_3,10H_2O$) or Glauber's salt.

Expt. 23.—*E*. Microcosmic salt, $Na(NH_4)HPO_4,4H_2O$, or Borax, $Na_2B_4O_7,10H_2O$.

Expt. 24.—*F*. Sulphur crystals, rock salt (does not melt).

Expt. 25.—*G*. Lead nitrate, $Pb(NO_3)_2$, rock salt ($NaCl$), Potassium chlorate ($KClO_3$).

Expt. 26.—*H*. Ammonium chloride, $(NH_4)Cl$.

Expts. 27 and 28.—The brown gas is dilute bromine vapour.

Expt. 28.—The charcoal should be well-burnt wood charcoal which has been roasted out of air contact shortly before the experiment. Keep in a desiccator and hand to students when they ask for it. If this precaution is not taken the experiment may not be successful as the charcoal on heating, after adsorbing the gas, may give very little or no brown gas but plenty of water vapour.

DEMONSTRATION 6

SEPARATION OF MIXTURES

There are many ways in which the constituents of mixtures may be separated. Of the methods given below all may be used for quantitative determinations, but you are only required to do one (as directed by the demonstrator) quantitatively. The others are to be studied so that you become acquainted with the methods.

Start the quantitative work *at once*, and while you are waiting for the various processes of filtration, drying, etc., to become complete, perform the other experiments Leave a space to finish the description of Expt. 31, and write up the account of each of the other experiments *as you perform them.*

EXPT. 30.—**Estimate the percentage of soluble and insoluble substance in the mixture A.**—One substance is soluble in water and the other is insoluble in water. Neither substance is decomposed by heat.

Clean and thoroughly dry the small beaker provided. Take it to the balance-room. See that your balance is correctly adjusted and swings properly. See that your weights are in order. Set the balance at " rest " Put the clean dry beaker on the left hand pan of the balance. Put a weight on the right hand pan by means of the forceps. Turn the handle so that the balance can swing. Add or remove weights till the pans of the balance swing evenly as indicated by the pointer, but always bring the balance to the position of " rest " before adding or removing anything. Weigh to the second place of decimals. Always replace a weight in its own proper place in the box if it is not being used on the pan of the balance.

Now write in your book:

Weight of the empty beaker = grams,

and (1) Count the weights on your pan.

(2) Count the value of the Spaces in your weight-box.

(3) Count the weights back into the box direct from the balance pan.

Each number may be entered on the left hand page of the practical note-book (1, 2 and 3 should be identical). Enter the weight of the beaker in your note-book. Now remove the beaker from the pan of the balance and put in it about 5 grams of the mixture *A* and weigh again. The difference between the first and the second weighings will give you the weight of the mixture *A* taken.

Now pour some distilled water on the mixture in the beaker, stir it up with a glass rod and then let it stand.

Weigh a filter paper.

Fold the filter paper carefully (1) into halves and then (2) into halves again so that it is in the form of four superimposed quadrants. Now open out one side so that the filter paper forms a cone.

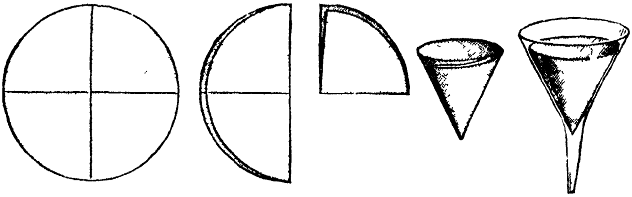


Fig 30.

Fit the cone in a glass funnel so that the edge of the filter paper is about half an inch below the glass edge of the funnel. *Never let the filter paper come up to or project over the edge of the funnel.* Pour some distilled water in the funnel. The water should pass through the paper and completely fill the tube of the funnel. No bubbles should be sucked between the paper and the glass, nor should any bubble be seen in the tube of the funnel. If these precautions are observed filtration will be much more rapid than if the paper is folded and fitted in a careless manner. Having fitted the paper correctly, put the funnel in a stand and a weighed evaporating basin underneath it. Take the glass stirring rod and put it vertically against the lip of the beaker and pour the liquid into the filter. The liquid will be found to run against the glass rod. All "dribbling" down the edge of the beaker is prevented. Never pour liquid into the paper to a greater height than ½ inch short of the edge of the paper.

When all the liquid has been poured off the residue, add some more water, stir, and pour through the filter paper. Repeat this. *This is called washing by "decantation."* Finally, pour the insoluble residue into the filter paper. It will be found hard to wash out the last portions of the solid. It may be done efficiently in this way. Hold the beaker and the rod in the left hand as shown in Fig. 32 and hold the wash-bottle in the right hand, manipulating the flexible jet with the index finger.

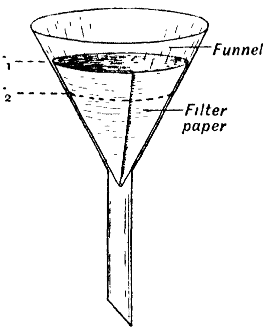


FIG. 31.—x_1. Height of filter paper edge. x_2 Maximum height of liquid in the paper during filtration.

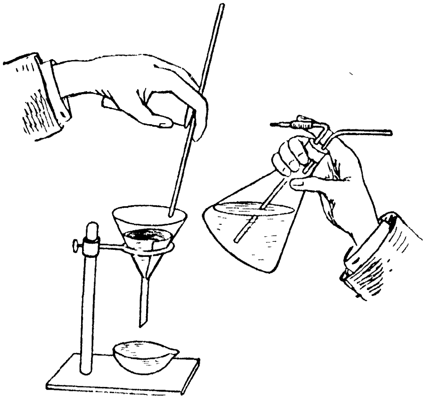


FIG. 32

When all the residue has been transferred to the filter paper see that the washings are free from salt by evaporating two or three drops on a small watch-glass held *by the bare fingers* a good distance above a clear Bunsen flame. Your fingers will tell you when the heat is likely to crack the glass. If the watch-glass is clean when dry, the sand has been washed free from salt.

When thoroughly washed, put the funnel in a filter dryer set in a sand-bath and gently heated by a Bunsen burner (Fig. 33 *A*).

See that the holes at the base of the cone are not choked with sand. Cover the funnel mouth with a piece of paper and leave till dry. Remove from the funnel and weigh.

Evaporate the collected washings in the weighed evaporating basin as shown in Fig. 33 *B*.

Direct evaporation on the sand-bath is difficult. The liquid usually spurts. When the evaporating basin is dry, **let it cool** and then weigh it.

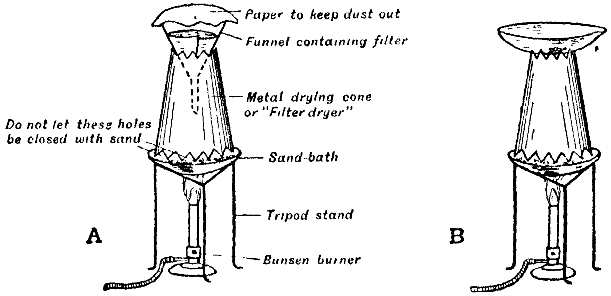


FIG. 33

Repeat weighing after heating till constant.

Write an account of all you do and enter your results thus :

Weight of the empty beaker = x grams.
Weight of the beaker and mixture = y ,,
∴ Weight of the mixture taken = $(y - x)$,,
Weight of the filter paper = a ,,
Weight of the filter paper + insoluble substance = b ,,
∴ Weight of the insoluble substance = $(b - a)$,,

Now $(y - x)$ grams of mixture contain $(b - a)$ grams of insoluble substance.

∴ 1 gram of mixture contains $\frac{(b - a)}{(y - x)}$ grams of insoluble substance.

∴ 100 grams of mixture contain $\frac{(b - a)}{(y - x)} \times 100$ grams of insoluble substance.

∴ *Required percentage of Insoluble substance is . . .* %. *Ans.*

Also weight of evaporating basin = c grams.
Weight of evaporating basin + soluble substance = d ,,
∴ Weight of the soluble substance = $(d - c)$,,

i.e., the percentage of soluble substance $= \frac{(d - c)}{y - x} \times 100$ . . . %.

If the percentages of insoluble and soluble substances add up to 100 there has been no loss or gain in the course of your experiment.

In addition to stating percentages of soluble and insoluble substances write down also the loss or gain per cent. obtained as a result of your analysis. Thus:

Required result {percentage of soluble substance = %
„ insoluble substance = %
Error = % (gain or loss).

Expt. 31.—**Both substances are soluble in water, but one is volatile and the other is fixed.**

The two bodies may be separated by sublimation, but the volatile body will be lost.

Heat some of *B* in a small crucible or capsule. Use the fume-closet.

Expt. 32.—**Both substances are insoluble in water; one is soluble in dilute acids, the other is insoluble in dilute acids.**

Digest *C* with dilute acid and, when the action has ceased, filter. Wash the residue very carefully and test the washings for acidity (litmus). If acids are used, especially sulphuric acid, *it is most important to wash the filter paper* quite free from acid, because if, in making a quantitative determination by this method, acid is left on the paper, the paper is corroded when it is dried. In case of sulphuric acid the paper is charred and the experiment spoiled.

Expt. 33.—**To separate the constituents of gunpowder.**—Taking advantage of the facts that—

(1) Carbon and sulphur are insoluble in water but nitre is soluble in water,

(2) Sulphur is soluble in carbon disulphide and carbon is insoluble in carbon disulphide,

You may separate the constituents of gunpowder, which is a mixture of nitre, carbon, and sulphur.

(1) Shake up the gunpowder with water. Filter. The residue is a mixture of carbon and sulphur. (If you wish to dry the mixture of carbon and sulphur do not use the drying cone—put the funnel in the steam oven. Write your name on the paper with which you cover the funnel.)

(ii) Extract the dry mixture of carbon and sulphur with carbon disulphide—*keep the carbon disulphide away from flames.* Filter. The residue is carbon. Wash with carbon disulphide. The sulphur may be recovered quantitatively by evaporation in air in a fume-closet. (Keep away from flames.)

Expt. 34.—**One constituent is combustible—the other is incombustible and non-volatile.** Heat the mixture in air (use the blow-pipe if necessary). The combustible substance will burn away; the incombustible substance will be left behind.

DEMONSTRATIONS

1. **Separation of gases** by taking advantage of their different rates of diffusion.

This is called " Atmolysis."

2. **Separation of two substances in solution** by taking advantage of the fact that one substance will pass through a certain membrane and the other substance will not pass through that membrane. Such a membrane is called a " semi-permeable " membrane.

The process of separation is called " Dialysis." The substance which passes through the membrane is called a " crystalloid "; the one which will not pass through the membrane is called a " colloid."

3. Centrifugalisation takes advantage of the different densities of substances in suspension in a liquid medium.

Notes to Demonstrators

It may be felt that there is too much work in this exercise for one day. The methods and processes are very important, and time would be well spent in devoting two demonstrations to this work, using, say, Expt. 30 as the quantitative exercise in the first lot of work, and Expt. 32 as the quantitative exercise in the second day's work. The rest of the demonstrations and exercises should be spread over two days.

For Expt. 30. *A*, use (i) common salt and sand, (ii) glass dust and common salt, etc.

Expt. 31. *B*, use ammonium chloride and common salt.

Expt. 32. *C*, use zinc powder and barium sulphate.

(Zinc dust with dilute sulphuric or hydrochloric acids give anomalous results. Dilute aqua regia as solvent gives the best results.)

C. Powdered marble and powdered glass (use dilute hydrochloric acid).

C. Magnesium powder and copper powder. (Use dilute hydrochloric or sulphuric acid.)

Expt. 33. *D* is gunpowder. Issue personally in small quantities, as required. You may substitute common salt for nitre and the experiment is still valuable but not dangerous.

Expt. 34. *E*. Mixture of silica and carbon.

Demonstration 1. Show the separation of the constituents of ammonium chloride vapour through a clay tube.

Demonstration 2. Dialysis of ferric hydroxide, or colloidal arsenious sulphide (add an *aqueous* solution of H_2S to an *aqueous* solution of As_2O_3; add *no* acid).

Demonstration 3. Use blood.

DEMONSTRATION 7

EXPT. 35.—*A* **is a mixture of two substances one of which is not decomposed by heat and is not volatile, and the other is decomposed by heat according to the equation** $2KClO_3 = 2KCl + 3O_2$, **leaving a non-volatile residue. Find the percentage of the decomposable body present.**

METHOD.—Wash the small porcelain crucible. Put it on the pipe-clay triangle and heat it. Allow it to cool till you can just bear your hand very near (but not touching) it, and then transfer to a desiccator (Fig. 34) by means of the iron tongs. When quite cool weigh it. Never touch the crucible with your fingers; always use the tongs. Now put about 1·5 grams of *A* in the crucible and weigh again. *Enter the weights directly into your note-book. Do not use scrap paper.* Put the crucible back in the desiccator by means of the tongs, and carry it back to your bench. Remove

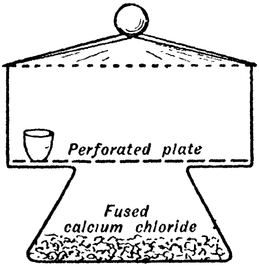


FIG 34.

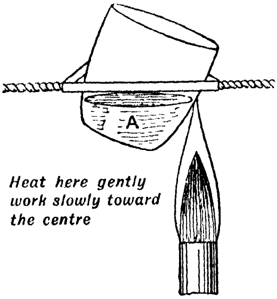


FIG. 35.

the crucible from the desiccator (using the tongs) and put it slantwise on the pipe-clay triangle.

Hold the Bunsen burner in your hand and heat very gently at *first from the outside edge* (see Fig. 35). When the action at that point is finished heat a new portion. Do not put the burner full on under the crucible and leave it. The mass will spurt and your experiment will be ruined. Taking proper care, excellent results will be obtained.

When all the action appears to have ceased, heat the crucible for a short time on the foot blow-pipe. If soot has deposited on the crucible *burn it off* with a fine blow-pipe flame. *Do not wipe it off. Let the crucible cool* till you can just bear your hand very near (but not touching) the crucible. Transfer to the desiccator (use the tongs). Allow it to finish cooling. When quite cool, weigh it.

Repeat heating, cooling and weighing till weight is constant.

Write an account of exactly what you do and enter your result thus :—

Loss of weight is due to the loss of oxygen according to the equation

$$2KClO_3 = 2KCl + 3O_2$$
$$2(39 + 35{\cdot}5 + 48) = 2(39 + 35{\cdot}5) + (3 \times 16 \times 2)$$

i.e. 245 grams of potassium chlorate would lose 96 grams in weight on heating, because that is the amount of oxygen which can be driven off from 245 grams of potassium chlorate.

Data :—

Weight of crucible = x grams.
Weight of crucible and *A* = y ,,
Weight of *A* taken = $(y - x)$,,
Weight of crucible and residue = z ,,
Weight of crucible and substance *A* = y ,,
Loss in weight = Oxygen driven off = $(y - z)$,,

Now 96 grams of oxygen represent 245 grams of $KClO_3$.

$\therefore$ 1 gram of oxygen represents $\frac{245}{96}$ grams of $KClO_3$.

and $(y - z)$ grams of oxygen represent $\frac{245 \times (y - z)}{96}$ grams of $KClO_3$.

This is the amount of $KClO_3$ in $(y - x)$ grams of *A*.

Weight of $KClO_3$ in $(y-x)$ grams of A $= \frac{245}{96} \times (y-z)$ grams.

∴ Weight of $KClO_3$ in 1 gram of A $= \frac{245}{96} \times \frac{y-z}{y-x}$,,

∴ Weight of $KClO_3$ in 100 grams of A $= \frac{245}{96} \times \frac{y-z}{y-x} \times 100$,,

$=$ . . . . . . ,,

∴ Required percentage of decomposable body in the mixture A is . . . %. *Ans.*

Notes to Demonstrators

Use $KClO_3 + Fe_3O_4$ or $KClO_3$ + glass dust.

Any suitable mixture may be given, due regard being paid to the fact that (1) the result must be quantitative and correctly represented by a chemical equation, (2) there should be no interaction between the two substances used.

DEMONSTRATION 8

PREPARATION AND PROPERTIES OF OXYGEN

EXPT. 36 —**Preparation of oxygen.**—Set up the apparatus shown in the diagram (Fig. 36) and make a sketch of it in your note-book. Write an account of all you do.

Into the test-tube put some of the given mixture of potassium chlorate and manganese dioxide. (See Expt. 94, page 98.) Shake the tube until the mixture lies along the tube as shown in the figure, but be careful not to let it come into contact with the cork.

Use small collecting jars.

Note that the tube is tilted with its mouth slightly downwards. Heat the substance at the end of the tube near the cork first and gradually work backwards towards the round end.

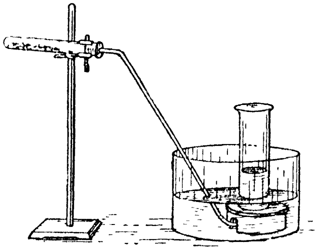


FIG. 36

In the following experiments USE SMALL QUANTITIES.

Observe the properties of the gas.

Write out the results, etc., in the form of a table arranged in three columns.

Experiment	*Observation.*	*Inference*
Write in this column all that you do	Write in this column all that you observe with your senses.	Write in this column the conclusion you draw from the observations made.

In the present case.

Experiment.	*Observation.*	*Inference.*
I examined the gas.	It is colourless	
I breathed the gas.	It has no taste. It has no odour.	
I shook the gas up with some blue litmus solution.	No change.	The gas is not an "acid."
I shook the gas up with some red litmus solution.	No change.	The gas is not alkaline in reaction.
And so on.		

Expt. 37.—**Properties of oxygen.**—(*a*) The gas is colourless.

(*b*) The gas is tasteless.

(*c*) The gas is odourless.

(*d*) Shake up some blue and red litmus solution with the gas. What happens? What conclusions do you draw from what you see?

(*e*) Shake up the gas with lime-water. What happens?

(*f*) It is slightly soluble in water.

(*g*) Put a glowing piece of wood into the gas. Does the gas burn? Does it support combustion?

Expt. 38.—**Combustion of carbon.**—By means of a deflagrating spoon put some glowing carbon into the gas. After any action has ceased shake some lime-water up in the cylinder (Fig. 37).

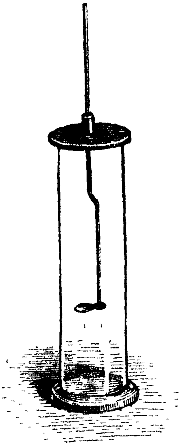


Fig. 37.

Expt. 39.—**Combustion of sulphur.**—Heat some sulphur in a deflagrating spoon. When just burning with a lambent flame, thrust the deflagrating spoon into the cylinder. Describe the physical properties of the substance formed.

Expt. 40.—**Combustion of iron.**—Put a little sand on the bottom of one of the cylinders of the gas. Fasten some iron wire to the deflagrating spoon. Make the wire red hot and plunge quickly into the cylinder. The wire burns.

In experiments 38, 39, 40 we have illustrations of the combustion of element oxygen with other elements. Compounds so formed are called oxides. In Expt. 38 carbon dioxide, in Expt. 39 sulphur dioxide, and in Expt. 40 iron oxide were formed. The process is called " oxidation."

Compounds which are composed of two elements only are called " binary " compounds. The names of such compounds usually end in " *ide*."

In the above cases (Experiments 38, 39, 40) compounds of carbon, sulphur and iron were formed by direct combustion. When a compound is formed by the direct union of its component elements it is said to be " synthesised." The process is called " synthesis."

Test for oxygen.—It is colourless, tasteless, odourless gas which supports combustion (compare nitrous oxide, page 109).

Expt. 41.—(*a*) **Heat some crystals of potassium permanganate alone.** Show that oxygen is given off. The potassium permanganate has undergone chemical change. Before the experiment the permanganate gave a purple solution in water. After heating, the residue gives a green solution in water and also a black substance insoluble in water.

(*b*) **Heat potassium chlorate alone.** Describe carefully all that happens. Is oxygen given off ?

(*c*) **Heat some of the yellow substance with strong sulphuric acid.** Describe all that happens. Is oxygen given off ?

DEMONSTRATIONS

(i) Oxygen is absorbed by a solution of pyrogallic acid in caustic soda.

(ii) Preparation of ozone by passing a silent electric discharge through air. The yield is improved by keeping the air cool. Draw a sketch of your apparatus in your note-book.

The action of ozone on potassium iodide will be shown.

Notice the peculiar smell of ozone.

Ozone is completely converted into oxygen by heating.

Note to Demonstrators

Expt. 41 (*c*). The yellow substance is potassium bichromate.

DEMONSTRATION 9

PREPARATION AND PROPERTIES OF HYDROGEN

EXPT. 42.—**Preparation of hydrogen.**—Write an account of all you do. Draw a diagram of the apparatus used (Fig. 38).

Fit up the apparatus as shown in the above figure. Be sure that all tubes are rounded off before pushing them through the corks or into the rubber tubing.

Make certain that the apparatus is air-tight by pouring water over the corks and then, having closed the thistle funnel by the palm of the hand, blow through the delivery tube *B*. If no bubbles come from the corks, etc., the apparatus is air-tight.

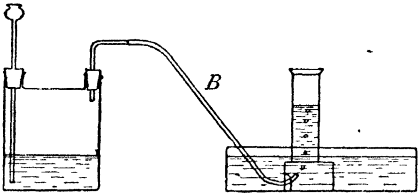


FIG. 38.

NEVER PATCH DEFECTIVE WORK WITH WAX. Take out the faulty piece and remake it.

Put some zinc in the Woulfe's bottle and pour a little water on it. There should be sufficient to seal the end of the thistle funnel. Add to it some dilute hydrochloric acid (one part of concentrated acid to four parts of water). If no action takes place add a few drops of copper sulphate solution through the thistle funnel. Chemical action will now commence and hydrogen gas will be given off. Notice that the liquid in the Woulfe's bottle gets hot. This heat is evolved as a result of the chemical action which is taking place. Keep the delivery tube, and, in fact, the whole apparatus, away from a naked flame.

Allow the action to proceed for two minutes, then collect some of the gas in a test-tube over water. Apply a match to the mouth of the tube. If an explosion takes place the hydrogen is contaminated with air. Keep testing the gas until, on applying a match to the test-tube, the hydrogen burns quietly.

Now collect several cylinders of gas.

Apply a light to the delivery tube. The gas burns.

Important Note.—If you wish to add more acid, FIRST BLOW OUT THE FLAME at the jet.

If you do not observe this precaution a *dangerous explosion* will take place. This is because, when adding the acid, some bubbles of air are dragged into the Woulfe's bottle and an explosive mixture is formed.

Do not relight the jet without testing the gas again in a test-tube as described above.

EXPT. 43.—**Observe the following properties.**—*Tabulate your results.* (See page 42.)

(*a*) The gas is colourless.

(*b*) " " " tasteless.

(*c*) " " " odourless.

(It is just possible that the sample of the gas prepared by you may have a faint smell. This is due to impurities in the zinc. Pure hydrogen has no odour at all.)

(*d*) Plunge a lighted taper in an inverted cylinder of the pure gas. The taper is extinguished, but the gas burns at the mouth of the cylinder. It is not a supporter of combustion, but it is combustible. Notice the steam on the walls of the cylinder.

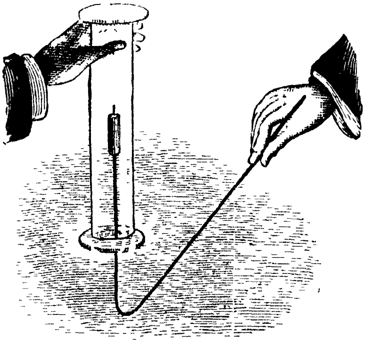


FIG. 39.

(*e*) Show that the gas is lighter than air by pouring the gas upwards.

Take a test-tube full of hydrogen and place its mouth under the mouth of an inverted test-tube full of air.

Remove the upper test-tube and apply a lighted match to its mouth. An explosion will take place showing that hydrogen has flowed upwards and mixed with the air in the upper tube. Hydrogen can be collected by upward displacement of air. (Fig. 40.)

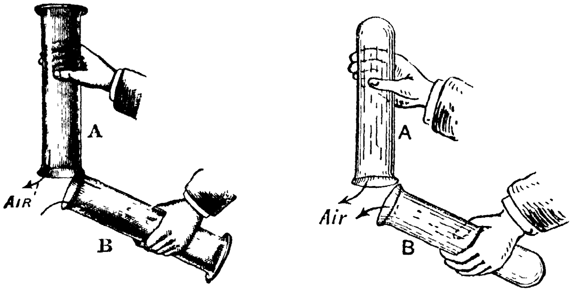


FIG. 40.

(*f*) The gas is not appreciably soluble in water.

EXPT. 44A.—**Hydrogen is a reducing agent.**—You are given a small tube containing copper oxide—*i.e.* the compound of the metal, copper, with the gas, oxygen. The substance is a black powder. Connect this tube to the delivery tube from your Woulfe's bottle. As soon as pure hydrogen is passing through the whole apparatus (test as before) apply heat to the tube containing copper oxide. Notice the change that takes place. A reddish residue remains in place of black powder. It is metallic copper. At the end of the tube remote from the generator will be seen drops of liquid. Put a little anhydrous copper sulphate on that liquid. The copper sulphate turns blue. The liquid is water. (See Expt. 21 (*a*) page 28.)

In other words, hydrogen has robbed hot copper oxide of its oxygen and given us metallic copper and steam which, on cooling, condenses and becomes water.

This process is called " reduction."

The chemical change may be represented by an equation.

CuO	+	H_2	=	Cu	+	H_2O
Copper oxide (black powder)		Hydrogen (gas)		Copper (red metal)		Water (liquid)

If the substance to be reduced is dissolved in water it is not sufficient to bubble hydrogen gas through the solution. The substance will not be reduced unless the gas is generated *in contact with* the dissolved substance. The hydrogen is particularly active at the moment of its generation and is called " nascent hydrogen."

EXPT. 44B.—**Reducing power of "nascent" hydrogen.**—You are given a solution of a coloured substance. This liquid will turn colourless on reducing the dissolved substance.

(*a*) Pass hydrogen through the coloured liquid. Observe that there is no change.

(*b*) Add a piece of zinc to a little of the solution and then pour in about 20 c.c. of dilute sulphuric acid. A dilute solution of the coloured body will show you the bleaching action more quickly and effectively than a strong one. Lightly close the tube with the thumb and move the tube GENTLY up and down so as thoroughly to mix the solution. In a few minutes the solution will become quite clear, showing that the hydrogen in the nascent state is more active than the gas. The bleaching in this case is due to the reduction of the colouring matter.

In connection with experiments 44A and 44B, the attention of the student is directed to the fact that, although both experiments are designed to illustrate the reducing power of hydrogen, another lesson is to be learnt, *i.e.*, the result that you will get depends upon whether or not you satisfy the *conditions necessary for the reaction to proceed.*

This matter will be dealt with in detail in a later demonstration, but note that it is not enough for you to know that such and such reactions can take place. You must also know the *conditions* necessary for the reaction to proceed.

EXPT. 45.—**Preparation of zinc sulphate crystals.**—When the action in the bottle has ceased, filter off the solid residue and evaporate the solution in an evaporating basin until it is about one-third of the previous bulk.

Remove the basin from the burner and cover it with a piece of paper on which you have written your name. Give it, when cool, to the laboratory assistant. He will set it aside for you and return it to you next time you come for practical work.

You should find some white crystals in the basin. They will probably be acid in reaction. Filter them off and dissolve them in a little water. Evaporate down and again allow the basin to stand. Crystals of zinc sulphate will be formed. Filter off. Dry on a porous plate or between filter papers. Show them to the demonstrator. Make a sketch of a good crystal.

DEMONSTRATIONS

1. The demonstrator will explain to you the precautions necessary for collecting and working with hydrogen.

2. **Detonating gas.**—A mixture of two volumes of hydrogen and one volume of oxygen is exploded. Carefully observe the precautions taken and note the thickness of the bottle used for the experiment.

3. **The Chemical Harmonicon.**—Hydrogen is generated in a flask provided with a long tube *A* (Fig. 41). The gas is ignited at the end of the tube and then the tube is passed into a wide tube *B*. A musical note is emitted. The explanation is this:—The hydrogen does not burn steadily. A series of small explosions takes place. Each explosion sets up longitudinal waves in the tube. The vibrations are sufficiently rapid to produce a musical note. The larger the number of vibrations in a given interval of time the higher the pitch of the note emitted. The pitch of the note can be varied by altering the position of the burning jet in the tube *B*.

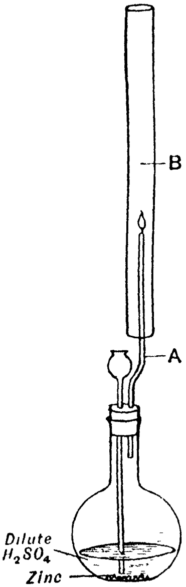


FIG. 41.

4. **Hydrogen gas is a conductor of heat.**—The apparatus illustrated in Fig. 42 is used to show this property of hydrogen gas.

(*a*) Pass an electric current through the wire when the tube is full of air. The wire glows.

(*b*) Pass an electric current of the same strength as in (*a*) through the wire when the tube is full of hydrogen.

The wire does not glow because the heat is taken away by the conductor of heat—hydrogen.

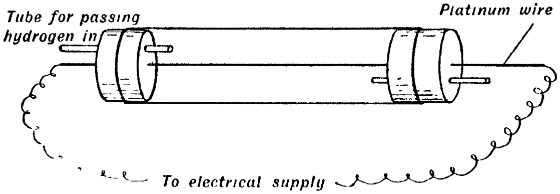


FIG. 42.

N.B.—See that the tube is full of *pure* hydrogen, otherwise, when the current is passed, an explosion may occur.

Note to Demonstrators.

Expt. 44B.—The coloured liquid is very dilute potassium permanganate solution.

DEMONSTRATION 10

EXPT. 46.—**Determination of the volume of gas evolved in a given reaction.**—Action of hydrochloric acid on a given metal.

Take a 4-oz. bottle such as is used for solid chemicals and fit it with a cork. Wrap the cork in paper and press it by rolling it on the floor under the sole of the foot. Select a piece of glass tubing and bore a hole in the cork to suit the size of the tube. Bend the tube as shown in the figure *AB*. The exact length of *AB* taken will vary with bottle used. Draw out the end *B* so that its bore is about half the former diameter and then bend it vertically upwards.

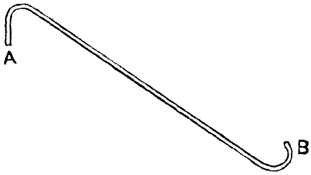


FIG. 43.

Pass the end *A* through the hole in the cork and draw it out and bend it at right angles so that the bend lies in a plane at right angles to the bend at *B*.

Fit the cork in the bottle and see that the apparatus is air-tight. Select a small test-tube which will just go inside the small bottle. Weigh some of the given substance on a watch glass. Put the substance in the bottle and weigh the watch glass again. The difference in these two weighings gives the weight of the substance used. Now pour about 30 c.c. of water on the substance. Fill the small test-tube with hydrochloric acid and gently slip it into the bottle without allowing any of the acid to spill. Fit in the cork and again test to see that it is air-tight. Now place the apparatus so that the angle *B* is under a jar inverted in a trough of water (Fig. 44). Use a small gas cylinder. Let the apparatus stand for a minute or two, then, holding the bottle by its neck or by the projecting portion of the cork, tilt the bottle sideways, keeping *B* under the cylinder. The cylinder should be supported by a clamp, not by a beehive shelf, as the latter has a way of collecting a certain amount of gas in it, and it is difficult to recover the gas. The bottle should be tilted in such a manner that the bend at *A* points upwards, *not downwards.*

Take care not to warm any parts of the apparatus containing gas by holding them in your hands.

When all action has ceased close the cylinder by a shallow dish or glass plate and transfer it to a glass basin or cylinder holding it all the time by means of a clamp. If you have not got a clamp wide enough to hold the cylinder take several folds of tough paper and fold them into a strip. Put the strip round the cylinder and tightly pinch the free ends (Fig. 68, page 217).

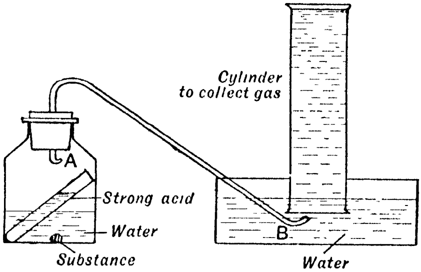


FIG 44.

Hold the cylinder so that the level of water inside it and outside is the same, and then stick a label on the outside of the cylinder at the level of the water.

This procedure is adopted to avoid the necessity of applying a correction for the difference in the heights of water inside and outside the cylinder.

Remove the cylinder from the water and measure its volume up to the level of the label with the help of the burette and pipette as described in Demonstration No. 4, page 21.

Since there is no hydrostatic pressure, the pressure of the gas inside the cylinder is made up of two factors (1) the pressure of the hydrogen, (2) the vapour pressure of the water at the temperature of the laboratory. These two together are equal to the barometric pressure at the place where experiment is being performed.

i.e., Barometric pressure = vapour pressure + gas pressure.

∴ Gas pressure = barometric pressure − vapour pressure.

Read off the barometric pressure from the barometer in the balance room. Note the temperature of the laboratory and find from Appendix II., page 271, what is the pressure of water vapour at that temperature. *Write down all the data at the moment you observe them.*

Write out the data thus:—

Weight of watch glass and metal = m grams.
Weight of watch glass and residue = m' ,,
∴ Weight of metal taken = $(m-m')$,,
Volume of the gas observed = V. c.c.
Temperature of laboratory = T° C.
Pressure of aqueous vapour at T° C. = b mm. Hg
Barometric pressure = B mm. Hg
∴ The gas pressure = $(B-b)$ mm. Hg

By Boyle's law we know that the volume of a gas varies inversely as the pressure to which it is subjected.

∴ If the gas occupies V c.c. at a pressure of $(B-b)$ mm. Hg, its volume at normal pressure (760 mm. Hg) will be $\left(V \times \frac{B-b}{760}\right)$ c.c.

By Charles' law a gas expands by $\frac{1}{273}$ of its volume; for every degree Centigrade its temperature is raised above 0° C. The temperature of the gas is T° C.

∴ The volume of the gas is $\frac{273+T}{273}$ times the volume it would occupy at 0° C.

∴ To find what its volume would be at 0° C. the volume must be multiplied by $\frac{273}{273+T}$.

Applying both corrections we get

$$\text{Volume of gas at N.T.P.} = \left(V \times \frac{B-b}{760} \times \frac{273}{273+T}\right) \text{ c.c.}$$

Weight of metal which gives this amount of gas is $(m-m')$ grams.

∴ Volume of gas evolved by one gram of the metal is

$$\frac{1}{(m-m')} \times \left(V \times \frac{B-b}{760} \times \frac{273}{273+T}\right) \text{ c.c.} = \ldots \text{ c.c.} \quad \textit{Ans.}$$

1. Do not try to learn this formula by heart. If you understand how it is arrived at you can always work it out.

2. If zinc is used, add a little copper salt to the concentrated hydrochloric acid before putting the acid in the test-tube.

DEMONSTRATION 11

WATER

Boiling point at 760 mm. mercury pressure = 100° C.
Freezing point at 760 mm. mercury pressure = 0° C.
Water is colourless, tasteless, and odourless.

EXPT. 47.—**Distilled water leaves no residue on evaporation.**—Evaporate some distilled water (*A*) to dryness in a glass basin. Heat the glass basin by means of a water-bath. There is no residue.

EXPT. 48.—**Tap water on evaporation leaves a residue.**—Now evaporate some tap water to dryness in the same way. A whitish residue remains.

EXPT. 49.—**Ordinary water contains dissolved gases.**—Take a 500 c.c. flask and fit it with a tight cork. Bore a hole in the cork and fit into it a glass tube bent as in Fig. 45. The end should be flush with or slightly inside the cork (do not forget to round off the edges of the tube after cutting it).

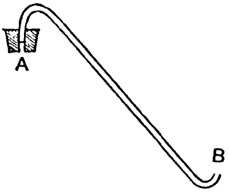


FIG. 45.

Put a few glass beads in the flask and then fill it *and the delivery tube* with tap or well water. The tube may be filled by putting *B* under water and sucking at *A* (Fig. 45). When the tube is filled with water close the end *B* with index finger and push the cork *A* into the neck of the flask, which has been previously filled to the brim with water. It will be found that it is quite easy to exclude all air.

Fit the flask into the retort-stand and dip the delivery tube under water in a pneumatic trough. Place a graduated cylinder over the mouth of the delivery tube and fasten it with a ring or padded clamp (Fig. 46).

Heat the flask and continue heating until the water in the flask has boiled for three minutes. When no more bubbles collect, the cylinder should be moved away from the delivery tube and then the gas turned off. Water will rush back into the flask owing to the condensation of the steam in the flask. Find the exact volume of the flask up to the cork and calculate what volume of gas would have been evolved by heating 100 c.c. of the water.

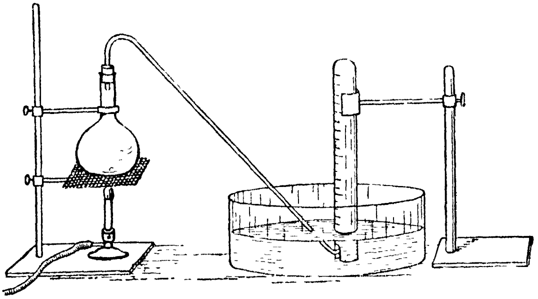


FIG. 46

EXPT. 50.—**Water as a solvent.**—Find out whether the given substances are soluble in water or not by shaking up each in turn with distilled water. Filter the liquid and evaporate some to dryness in a clear glass basin on a water-bath. Note if there is any change in temperature when the given solids are shaken up with water. Sometimes the volume of the mixture of two substances is not the same as the volumes of the unmixed substances.

Take a known volume of alcohol. Mix it with an equal volume of water. Do you observe any change in volume ? If so calculate the percentage change.

EXPT. 51.—**Show that the boiling point of water is raised by having a substance dissolved in it.**—For this purpose use the solution supplied by the demonstrator.

For this experiment find the boiling point of the liquid with the thermometer *in the liquid, not in the vapour.* The vapour only consists of steam, and so would indicate the boiling point of the *solvent* water. We are trying to find the boiling point of the *solution.*

EXPT. 52.—**Examine the given samples of water.**—Dirty water contains (i) suspended impurities (these may be separated by *filtration*, Expt. 30, page 31); (ii) dissolved impurities (these may be separated by *distillation,* Expt. 12, page 16).

If the water gives a yellow or brown coloration with "Nessler's reagent," it is contaminated and unfit for drinking.

Test *all* the given samples by this test.

HARD AND SOFT WATER

Pure water readily gives a frothy mass of bubbles called a "lather" when shaken up with a soap solution. Water which readily gives a lather with soap solution is said to be "*soft.*"

Water which, instead of giving a lather with soap solution, causes the soap to separate as a curd or scum is said to be "*hard.*" This "*hardness*" is due to the presence of dissolved substances. It is of two kinds—"temporary hardness" and "permanent hardness."

If the hardness can be removed by simply boiling the water it is called "temporary" hardness. This is due to the fact that the substances causing the hardness are decomposed by heat and are removed from the solution partly in the form of gas, partly as a precipitate. Either process removes the substance from the "sphere of action" and thus stops any further action on the dissolved soap solution.

"Permanent hardness" cannot be removed by boiling.

EXPT. 53.—**Find the relative degrees of hardness of each of the given samples of water.**—(*a*) Put your soap solution into a burette. Take 100 c.c. of distilled water in a flask. Add 0·5 c.c. of the given soap solution. Close the mouth of the flask with your thumb. Shake up vigorously. If no lather forms add 0·5 c.c. more of the soap solution and repeat until a lather is formed which lasts 3 minutes. Say it requires x c.c. This is the quantity of soap solution required to give a permanent lather with pure water.

(*b*) Now take 100 c.c. of your given sample of water and put it to boil. In the meantime take another 100 c.c. of the same sample and add x c.c. of soap solution. If a permanent lather forms the water is "soft." If not, continue adding soap solution 0·5 c.c. at a time. Shake up after each addition until a permanent lather is obtained. Suppose the unboiled sample requires y c.c. of soap solution; $(y - x)$ c.c. gives a measure of the "total hardness."

(*c*) Cool the boiled water by holding the bulb of the flask under the cold-water tap and make the volume up to 100 c.c. with distilled water. (Some water will have been lost as steam during the boiling.)

Again add soap solution 0·5 c.c. at a time until a permanent lather is obtained on shaking.

Suppose z c.c. are required to secure a permanent lather—

Then total hardness is indicated by $(y - x)$.

Permanent hardness is indicated by $(z - x)$.

Temporary ,, ,, ,, ,, $(y - z)$.

Tabulate your results for the given samples.

Sample.	Total hardness	Permanent hardness.	Temporary hardness
Distilled (*A*) ..			
Tap (*B*)			
Well (*C*)			
Puddle (*D*) ..			
,,			
,,			
,,			

Water is a compound of hydrogen and oxygen. Its formula is H_2O, which shows that two atoms of hydrogen are in combination with one of oxygen.

If one of these atoms of hydrogen is replaced by a metal a compound called a hydroxide is formed. All hydroxides contain the monovalent group "OH."

EXPT. 54.—**Tests for the hydroxyl group** (*i.e.* **ion) in solution.**—If the hydroxide is soluble in water the following reactions indicate its presence.

(*a*) Pink litmus solution is turned blue.

(*b*) Phenolphthalein solution is turned pink.

(*c*) On adding a solution of the hydroxide to ferric chloride solution a brown precipitate is formed. This precipitate is soluble in dilute acids.

Soluble hydroxides give similar precipitates of insoluble hydroxides with other salt solutions, but only one typical instance is given here.

An example of the direct formation of an hydroxide is illustrated by the action of sodium on water.

$2Na$	$+$	H_2O	$=$	$2NaOH$	$+$	H_2
Sodium	acts on	Water	and gives	Sodium hydroxide	and	Hydrogen

Water is an oxide of hydrogen.

There is a second oxide of hydrogen called hydrogen peroxide (H_2O_2).

EXPT. 55.—**To test for hydrogen peroxide.**—To the given solution of hydrogen peroxide add a few drops of dilute sulphuric acid. Now pour some ether into the test-tube. The ether will form a layer of liquid on the surface of the aqueous solution. Now add two or three drops of potassium chromate (or potassium bichromate) solution. Shake up the tube. A beautiful blue colour develops and the ether dissolves the blue substance, giving the ethereal layer a blue colour.

Some peroxides give this test also, but not all.

DEMONSTRATIONS

1. All gases are not soluble in water to the same extent. You will be shown specimens of several gases, and the fact that their degrees of solubility differ will be demonstrated.

2. If the solutions of certain solids are boiled, a precipitate comes down. The precipitate redissolves when the solution is cooled.

Such substances are less soluble in hot water than in cold water.

3. The action of the steam ovens and the continuous "still" will be explained.

4. The demonstrator will explain and illustrate to you what is meant by "vapour pressure."

Make notes on the demonstrations as well as on the experiments actually performed by yourself.

Notes to Demonstrator

Expt. 50. Give insoluble as well as soluble bodies, and liquids as well as solids.

Expt. 51. Give a saturated solution of common salt, or better, a strong solution of calcium chloride.

Expt. 52. Nessler's reagent is made by dissolving 16 grams of potassium iodide in 150 c.c. of distilled water. Reserve 10 c c. of this solution and add, with constant stirring, the remaining 140 c.c. to a cold saturated solution of mercuric chloride. A slight precipitate should remain after all the potassium iodide has been added. Add potassium iodide from the 10 c.c. reserved until the precipitate redissolves. Dissolve 100 grams of caustic potash in 150 c.c. of water, and when cool add this solution to the one prepared above. Dilute the solution to 500 c.c. and store in a brown bottle in dark cupboard.

Expt. 54. Dissolve oleic acid in alcohol. Add phenolphthalein solutions, add KOH in alcohol (strong solution) till the oleic acid is neutralised (faint purple colour with phenolphthalein). Dilute with water.

Expt. 55. Give MnO_2 and BaO_2.

DEMONSTRATION 12

SOLUBILITY

EXPT. 56.—**To determine the solubility of a given substance in water at the temperature of the laboratory.**—You are given sodium chloride crystals. Finely powder some of the crystals in a mortar. To powder a substance with a pestle, do not bang the pestle on to the substance. It usually causes the substance to shoot out of the mortar. It will be found more advantageous to press and grind the substance by holding the mortar firmly in the left hand and the pestle in the right and giving the pestle a twisting motion while pressing firmly.

Put some of the powder in a flask and shake it up with distilled water. Stand the flask on one side and shake it at intervals. Clean an evaporating basin, warm it, and then allow it to cool in a desiccator if available. Transfer to the balance and weigh it. Put the weight down *in your note-book*. Pour about 20–30 c.c. of the solution through the filter paper into the weighed evaporating basin. There must be some of the solid substance in contact with the solution all the time until the solution is poured through the filter paper into the weighed evaporating basin.

Take the temperature of the solution. Again weigh the evaporating basin and solution. Now evaporate the solution to dryness. This must be done carefully and all spitting or spurting must be avoided or serious errors will occur.

Do not try to rush the evaporation by over-heating the evaporating basin.

The evaporation may be done—

(1) By heating the solution on a water-bath.

(2) By heating the solution on a sand-bath.

You must watch very carefully that the temperature is not too high or spurting will occur.

(3) By heating the basin on a cone set upon a sand-bath as explained in detail in Demonstration 6 (page 34, Fig. 33 *B*).

After cooling the evaporating basin till the hand can be borne close to it, allow the final cooling to take place in a desiccator. Weigh the crucible and residue. Heat, cool and weigh again. Repeat the heating, cooling and weighing until the weight is constant.

Data :—

Weight of evaporating basin = W grams.
Weight of evaporating basin and solution = w ,,
Temperature of the solution (laboratory temp.) = t° C.
Weight of evaporating basin and residue when constant = w_1 ,,
∴ Weight of dissolved substance = $(w_1 - W)$,,
Weight of solvent (water) = $(w - w_1)$,,

∴ Weight of substance dissolved by $(w - w_1)$ grams of water $= (w_1 - W)$ grams.

∴ Weight of substance dissolved by 1 gram of water

$$= \frac{(w_1 - W)}{(w - w_1)} \text{ grams.}$$

∴ Weight of substance dissolved by 100 grams of water

$$= \frac{(w_1 - W)}{(w - w_1)} \times 100 \text{ grams.}$$

Required result:

100 *parts by weight of water at* t° *C. dissolve . . . . parts by weight of sodium chloride. Ans.*

DEMONSTRATION 13

PREPARATION AND PROPERTIES OF HYDROCHLORIC ACID

EXPT. 57.—**Preparation of hydrochloric acid gas.**—*The fumes of this gas are very objectionable and irritating, so the experiment should be performed in a fume closet.*

Fit up a flask with a cork bored with two holes through one of which passes a thistle funnel and through the other a delivery tube. The thistle funnel dips nearly to the bottom of the flask (Fig. 47). See that all the ends of the tubes are rounded off and that the apparatus is air-tight.

The delivery tube should be long enough to reach nearly to the bottom of the cylinder.

It will be found easier to change the cylinders quickly if the arrangement shown in Fig. 47 is adopted. If the cylinders stand on the working bench it is difficult to remove the delivery tube from them quickly.

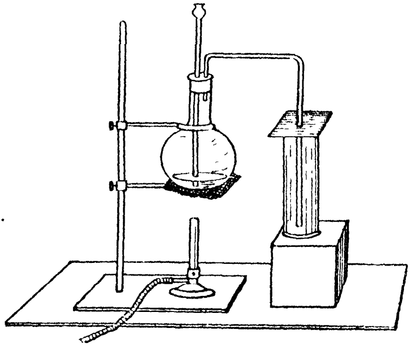


FIG. 47.

See that the cylinders you will use for collecting the gas are dry.

Put some small crystals of common salt in the flask and fit up the apparatus. Pour strong sulphuric acid through the thistle funnel. Hydrochloric acid gas will be evolved immediately. At first no heat is required, but when the evolution of gas slackens the flask should be *gently* heated with the Bunsen burner.

The reaction which takes place is represented by the equation:

$NaCl$	+	H_2SO_4	=	HCl	+	$NaHSO_4$
Sodium chloride	with	Sulphuric acid	gives	Hydrochloric acid gas	and	Sodium bisulphate

IN A FLASK *the reaction does* NOT *proceed to the formation of normal sodium sulphate.*

You can test when a gas cylinder is full by holding a piece of moist blue litmus paper near the mouth of the gas cylinder. When the cylinder is full the litmus paper turns pink.

To change the cylinder (1) remove the wooden block, (2) remove the cylinder and put a dry cover on it at once, (3) slip a new jar into position and support it by the wooden block.

Observe that the gas fumes when it comes into contact with air. This is due to the moisture in the atmosphere.

EXPT. 58.—**Properties of hydrochloric acid gas.**

Collect several cylinders of the gas and observe its properties.

Describe in your note-book all you do and see, etc.

Tabulate your results under three heads, "Experiment, Observation, Inference." (See Demonstration 8, page 42.)

(1) It is colourless.

(2) It has an intensely acid taste.

(3) It has a pungent, irritating smell.

(4) Plunge a lighted taper into a cylinder of the gas. Does it support combustion? Does it burn?

(5) Shake the gas up with blue litmus solution.

(6) Shake the gas up with lime-water.

(7) Throw a moist flower into the gas. Has the gas any bleaching action?

(8) Invert a cylinder of gas in a basin of water. Is the gas soluble in water? Test the water with litmus solution.

(9) Invert a cylinder of the gas over another cylinder in which a few drops of ammonia solution have been shaken up.

The white fumes which are formed are ammonium chloride.

NH_3	+	HCl	=	NH_4Cl
Ammonia		Hydrochloric acid		Ammonium chloride
(colourless gas)		(colourless gas)		(white solid)

Ammonium chloride is an "addition" product of ammonia and hydrochloric acid.

Sodium chloride is a "substitution" product of hydrochloric acid.

EXPT. 58A.—**Hydrochloric acid solution.**—Dissolve some of the gas in water by allowing *the delivery tube to remain a quarter of an inch above the surface of distilled water* in a test-tube while the gas is being generated in the flask.

Perform the following experiments with the solution:

(*a*) Add zinc to some of the solution. What happens? If a gas is given off, see if you can detect what it is.

(*b*) Add some of the solution to sodium carbonate. What happens? Give equation.

(*c*) Take a little of the strong solution and add to it some manganese dioxide in a test-tube. A coloured, pungent smelling gas called "chlorine" is evolved. This will be studied in the next demonstration. All peroxides give this reaction with hydrochloric acid.

MnO_2	+	$4HCl$	=	Cl_2	+
Manganese dioxide	with	Hydrochloric acid	gives	Chlorine	and

$MnCl_2$	+	$2H_2O$
Manganese chloride	and	Water

EXPT. 59.—**To test for hydrochloric acid.**—Add to the solution a solution of silver nitrate. A white precipitate of silver chloride is thrown down. This precipitate is soluble in ammonium hydrate. When the clear solution so formed is acted on by dilute nitric acid, the silver chloride is reprecipitated.

$AgNO_3$	+	HCl	=	$AgCl$	+	HNO_3
Silver nitrate	and	Hydrochloric acid (or any soluble chloride)	give	Silver chloride (white precipitate) insoluble in water, or dilute nitric acid, soluble in ammonia	and	Nitric acid

All acids are compounds of hydrogen—*e.g.*, Hydrochloric acid, HCl, sulphuric acid, H_2SO_4, nitric acid, HNO_3, etc. When the hydrogen of an acid is replaced by a metal (or a group of atoms equivalent to a metal) the body formed is called a "salt."

DEMONSTRATIONS

(1) The electrolysis of hydrochloric acid in a Hoffmann's apparatus will be shown to you. Draw a sketch of the apparatus. Carbon electrodes are used. See that hydrogen (test) and a new greenish coloured gas are evolved. This gas is called "chlorine."

N.B.—The solution in the limb which will contain the chlorine should be saturated with chlorine before starting the electrolysis. Do not saturate with chlorine the solution in the limb in which hydrogen will be collected.

(2) The apparatus by which a continuous stream of dry hydrochloric acid may be obtained will be shown to you. Make a sketch of it. From a dropping funnel concentrated hydrochloric acid is dropped upon strong sulphuric acid contained in a flask. Heat the flask gently if necessary. (See Fig. 48, Demonstration 14, page 70.)

(The mixture of sulphuric and hydrochloric acids after dilution may be used for the preparation of sulphuretted hydrogen in a "Kipp," or for the preparation of hydrogen.)

WHAT IS AN ACID?

An Elementary Idea of the Theory of "Ions"

A body carrying a charge of positive electricity will attract a body carrying a charge of negative electricity.

Suppose that we have a large fixed body charged with positive electricity and that, in its neighbourhood, we have a small body charged with negative electricity and that this small body is free to move in space. This small negatively charged body will approach and finally touch the fixed positively charged body. When this takes place the small body will lose its negative charge and a certain amount of the positive charge on the fixed body will be neutralised.

A similar course of events will take place if a large negatively charged body is fixed and a small positively charged body is free to move in its vicinity.

If there is a *number* of mobile negatively charged bodies in the neighbourhood of a fixed positively charged body they will, one by one, come into contact with the positively charged body and the charge on the latter will be diminished. Similarly, the charge on a fixed negatively charged body will decrease in the presence of a number of mobile positively charged bodies.

Suppose that we have a source of energy which will keep these fixed bodies charged with constant amounts of positive and negative electricity respectively (even though they are liable to lose part of their charge from any cause). If the source of energy is due to a chemical reaction the apparatus producing the energy is called a "battery" and the positively and negatively charged bodies are called the positive and negative poles of the battery respectively. Let these two poles dip into a vessel containing a solution of hydrochloric acid in water. They are now called "electrodes." The positive pole is called the anode and the negative pole is called the cathode. In the case under consideration the electrodes would be made of carbon. When these carbon electrodes, connected to a battery, are put into the solution of hydrochloric acid in water we see that (1) hydrogen appears at the cathode and (2) a gas, which proves to be chlorine, appears at the anode.

If, before putting the electrodes in the hydrochloric acid, the solution had been examined, we should not have found more hydrogen in one part of the solution than another. The natural interpretation of the observed facts is that the placing of these charged electrodes in the solution has caused the hydrogen of the acid to move towards the cathode. It appears from this that the hydrogen present exists in the form of small particles, each of which carries a charge of positive electricity. Similarly the chlorine exists in the form of small particles, each of which carries a small charge of negative electricity. These charged particles are called "ions" and are capable of movement in the solution.

Before the poles of the battery are put into the solution these ions exist in the solution and wander aimlessly about. When the poles of the battery (electrodes) are inserted, the motion of the charged particles (or "ions") is influenced by the directive action of the charged electrodes.

On reaching the electrode the ion parts with its charge, neutralising a portion of the charge on the electrode. The charge on the electrode is again brought up to strength by calling upon the reserve of electrical energy supplied by the battery.

When the ion of hydrogen loses its charge it possesses the property of an atom, and two atoms immediately combine to form a molecule of hydrogen. Several of the molecules accumulate and form what we *see*, viz. a bubble of hydrogen gas. A similar explanation applies to the formation of bubbles of chlorine gas.

This property of splitting into two or more electrically charged particles in solution is called "electrolytic dissociation," or "ionisation," and *any* solution which contains a particular ion will give the reactions peculiar to that ion. Now hydrochloric acid, when dissolved in water, splits up into two ions, *i.e.* hydrogen ions and chlorine ions.

The reactions of a solution of hydrochloric acid may be considered to be due to two causes: (1) the presence of hydrogen ions and (2) the presence of chlorine ions.

All solutions containing hydrogen ions will possess certain properties. Such solutions are called "acids." Hence the simplest definition of an acid is—*An acid is a body which, on solution in water, gives free hydrogen ions.*

All bodies which, on solution in water, give chlorine ions are called "chlorides" and give certain reactions—hence the test for a chloride in solution is really the test for chlorine ions. In general terms we may say that all tests for metals and acids in solution may be considered as the tests for the presence of certain ions.

In the case studied above, each of the ions carries what is called one unit charge, the hydrogen ion carries one such unit positive charge and the chlorine ion one unit negative charge, but an ion *may* carry more than one unit charge, *e.g.* calcium, barium, or strontium ions carry two positive unit charges each, the aluminium ion carries three positive unit charges, and so on.

The ions so far considered consist of one atom only (*i.e.* are monatomic), but an ion may consist of several atoms combined together and this group of atoms in combination behaves as a distinct body.

These groups of atoms, which possess distinct individuality and properties and which can be transferred from one compound to another, simultaneously retaining their characteristic properties, are called "radicals."

When these radicals exist in solution, and carry one or more unit charges of electricity, they are also called "ions."

Such ions may be negative and carry a negative charge, *e.g.* the $(NO_3)^{\cdot}$ ion, or "nitrate" ion, the $(OH)'$ or "hydroxyl" ion, or they may be positive and carry a positive charge, as, for example, the

$(NH_4)^{\cdot}$ ion, or "ammonium" ion. These ions may also carry more than one unit charge, *e.g.* the $(SO_4)''$, or "sulphate," ion carries two unit negative charges, the $(PO_4)'''$, or phosphate, ion carries three unit negative charges, and so on.

Every acid gives *hydrogen* ions when dissolved in water, hence the tests peculiar to a given acid will be the tests peculiar to the negative radical associated with the hydrogen of the acid in solution. When the hydrogen of an acid is replaced by a metal (or positive radical) a salt is formed. Hence the test for a salt in solution will consist of the tests for the ions of the metal PLUS the tests for the negative ion peculiar to the acid of which the given substance is a salt.

Thus the test for calcium chloride in solution comprises the tests for the calcium ion *together with* the tests for the chlorine ion.

IMPORTANT.—The following so-called "definitions" of an acid *are incorrect:*

(1) An acid is a body which turns blue litmus red. All soluble acids do this, but other bodies also do it.

(2) An acid is a body containing hydrogen which is replaceable by a metal. Sodium hydrate would be an acid under this definition!

$$\underset{\text{Sodium hydrate}}{2NaOH} \underset{\text{with}}{+} \underset{\text{Zinc}}{Zn} \underset{\text{gives}}{=} \underset{\text{Sodium zincate}}{Na_2ZnO_2} \underset{\text{and}}{+} \underset{\text{Hydrogen}}{H_2}$$

(3) An acid is a body which has a sour taste.

DEMONSTRATION 14

PREPARATION AND PROPERTIES OF CHLORINE GAS BLEACHING POWDER

EXPT. 60.—**Preparation of chlorine.**—Set up an apparatus identical with that used in the preparation of hydrochloric acid gas (*vide* Fig. 47, page 61). Smear the cork with melted paraffin wax, otherwise the gas will corrode it inside the flask.

Put a little water on the bottom of the flask and then add either (1) granulated manganese dioxide, or (2) a mixture of manganese dioxide, 3 parts, and common salt (sodium chloride) 2 parts.

Put the apparatus in a fume closet, as the gas which will be evolved is obnoxious and poisonous.—See that the apparatus is air-tight.

If you are using the first method pour strong hydrochloric acid down the thistle funnel. The action will be

$$\underset{\text{Manganese dioxide}}{MnO_2} \underset{\text{with strong}}{+} \underset{\text{Hydrochloric acid}}{4HCl} \underset{\text{gives}}{=} \underset{\text{Manganese chloride}}{MnCl_2} \underset{\text{and}}{+} \underset{\text{Chlorine gas}}{Cl_2} \underset{\text{and}}{+} \underset{\text{Water}}{H_2O}$$

If you are using the second method pour strong sulphuric acid down the thistle funnel.

Write equations for what happens.

If, by accident, you inhale the gas and feel any distress, go into the open air and breathe deeply. Call to the laboratory assistant for boiling water and breathe the steam. It will give you some relief.

EXPT. 61.—**Test the properties of chlorine.**

Write your report in tabular form.

Observe that the gas—

(1) has a greenish-yellow colour.

(2) has a peculiar and unpleasant smell.

(3) is soluble in water. Its solution is called "chlorine water."

(4) bleaches dry or wet litmus paper.

(5) bleaches indigo solution and coloured cloth and flowers which have been moistened with water.

(6) releases iodine from a solution of potassium iodide, $2KI + Cl_2 = 2KCl + I_2$. Iodine gives a *blue* coloration with starch solution.

(7) releases bromine from a solution of potassium bromide, $2KBr + Cl_2 = 2KCl + Br_2$.

(8) reacts with turpentine spread on a rag. Show that hydrochloric acid is formed as well as carbon, etc.

(9) reacts with Dutch metal, forming a soluble body.

(10) does not burn.

(11) supports combustion of certain substances.

The demonstrator will show you hydrogen burning in chlorine.

The tests for chlorine depend on the fact that—

1. It has a peculiar smell.
2. It has a greenish-yellow colour.
3. It has a bleaching action.
4. It releases iodine from potassium iodide solution.

The presence of the free iodine is shown by adding starch solution. A bright blue coloration indicates the presence of free iodine.

EXPT. 62.—**Test for peroxides** (*vide* also Expt. 55, page 57.)—Show that the given peroxides and other highly oxygenated substances give off chlorine gas when heated with concentrated hydrochloric acid.

When chlorine combines with another element the resulting compound is called a "chloride."

DEMONSTRATIONS

1. **Chlorine is a supporter of combustion.**—(*a*) The demonstrator will show you a jet of hydrogen burning in chlorine gas. The resulting body is called hydrogen chloride or hydrochloric acid gas.

The tests for the acid will demonstrate its presence. This is a synthetic method of preparing hydrochloric acid gas.

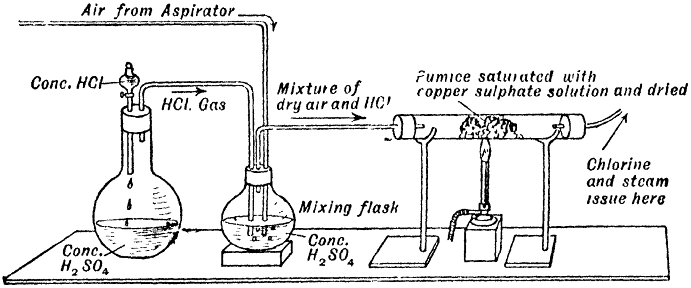
H_2	+	Cl_2	=	$2HCl$
Hydrogen	combines with	Chlorine	to give	Hydrochloric acid gas

(*b*) Antimony spontaneously bursts into flame when thrown into chlorine gas; a white solid (antimony trichloride) is formed.

$2Sb$	+	$3Cl_2$	=	$2SbCl_3$
Antimony	combines with	Chlorine	to give	Antimony trichloride

2. A laboratory demonstration of Deacon's process for the manufacture of chlorine will be given.

$4HCl$	+	O_2	=	$2H_2O$	+	$2Cl_2$
Hydrochloric acid gas	and	Oxygen	give	Water	and	Chlorine



Air from Aspirator
Conc. HCl
HCl. Gas
Mixture of dry air and HCl
Pumice saturated with copper sulphate solution and dried
Chlorine and steam issue here
Mixing flask
Conc. H_2SO_4
Conc. H_2SO_4

FIG. 48.

Note to Demonstrators.—To make indigo solution (1) dissolve indigo-carmine in water, *or* (2) warm 1 gram of indigo with 12 c.c. of fuming sulphuric acid. Stand aside till next day, then dilute with 20 volumes of water. In either case use a dilute solution of the reagent for showing the bleaching action of chlorine.

BLEACHING POWDER

EXPT. 63.—**To make a sample of bleaching powder.**—Take some quicklime and add a little water to it so as partially to slake it, but do not *wet* the lime. Remember that the chlorine carries over with it a certain amount of steam, and so the lime need only be partially slaked. The steam in the chlorine supplies the rest of the water requisite. Put this lime into the bottom of a gas cylinder and stir or shake up at intervals. Continue doing this until the colour of the gas in the cylinder remains greenish-yellow.

Notice that the lime gets hot. Keep it from over-heating by immersing the base of the cylinder in cold water in a trough or basin.

When the lime has ceased to absorb the gas (seen by the persistence of the greenish colour) pour out the whitish substance which is in the cylinder. Notice its peculiar smell. It is " bleaching powder " or the commercial substance " chloride of lime."

$Ca(OH)_2$	+	Cl_2	=	$Ca(OCl)Cl$	+	H_2O
Slaked lime	with	Chlorine	gives	Bleaching powder	and	Water

Mix some of the bleaching powder with water.

Allow the turbid liquid to settle and then pour off the clear solution. To this add a few drops of dilute hydrochloric acid and then a rag on which some ink has been spilt.

The ink stains will be " bleached."

Expt. 64.—**Tests for hypochlorous acid (HClO) and hypochlorite.**—When bleaching powder is dissolved in water, calcium chloride and calcium hypochlorite are present in the solution.

$2Ca(OCl)Cl$	+	Aq	=	$CaCl_2$	+	$Ca(OCl)_2$
Chloride of lime	in	Water	gives	Calcium chloride	and	Calcium hypochlorite

(1) Hypochlorites have a peculiar smell.

(2) The addition of dilute hydrochloric acid causes the evolution of chlorine gas. Show the presence of chlorine by potassium iodide–starch test.

(3) The solution acidulated with dilute hydrochloric acid has a strong bleaching action.

(4) Addition of cobalt nitrate causes the evolution of free *oxygen*. The action is catalytic (catalyst–cobalt oxide).

$$2Ca(OCl)_2 = 2CaCl_2 + O_2.$$

DEMONSTRATION

A little bleaching powder is taken in a test-tube and water is added to it, then a little hydrochloric acid. Now a small fragment of calcium carbide is thrown into the solution.

From the solution there issue bubbles of gas (a mixture of acetylene and chlorine) which spontaneously burst into flame.

DEMONSTRATION 15

CARBON

Carbon may be produced from certain naturally occurring "organic" bodies, *i.e.* (carbon compounds of animal or vegetable origin), by heating them in their natural state out of contact with air.

This is called "dry distillation," or destructive distillation.

EXPT. 65.—**Dry distillation.**—Fit up an apparatus like that shown in Fig. 49. From the test-tube *A*, which should be set so that it slants downwards slightly at the delivery tube end, leads a tube which passes into a second test-tube, *B*. This test-tube is set in a cylinder of cold water which will serve as a condenser for any portions of the distillate which exist normally in the liquid state at the temperature of the laboratory. This second test-tube is in turn provided with an outlet tube, which passes under another test-tube filled with water and immersed in a trough of water. In this test-tube are collected any gases produced during the distillation.

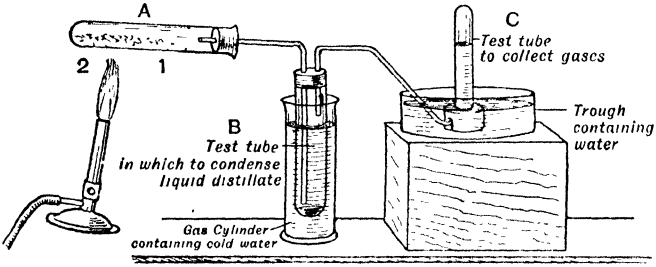

A
C
Test tube to collect gases
2
1
Trough containing water
B
Test tube in which to condense liquid distillate
Gas Cylinder containing cold water

FIG. 49.

In *A* chips of wood are placed. Leave a passage over the surface of the wood so that the vapours, etc., produced may be able to pass away freely.

Commence heating *A* at 1 and, as the mass inside chars, work the burner to the left.

Drive out as much air as possible before collecting any gas.

Repeat the experiment with feathers, rubber, etc.

Give an account of the physical properties, *e.g.*, solid, liquid, gas, colour, smell, solubility in water, acidity or alkalinity, etc. Show that you possess power of observation.

In the case of gases, colour, smell, presence of CO_2 inflammability, etc., should be noted.

Tabulate the result.

Substance heated.	Properties of the residue.	Properties of the distillate.	Properties of the gas
1. Wood .			
2. Feathers .			
3. Rubber ..			
4. Bones ..			

EXPT. 66.—**Allotropic modifications of carbon.**—1. You are given a sample of *coal.* Describe it. See that the coal occurs in layers and splits along the line of separation of these layers.

2. Describe the properties of *graphite.* See that it marks paper. It is the substance of which so-called " lead " pencils are made.

3. Describe a *diamond.* It is crystallised carbon.

4. You are given a rag soaked in oil. Put it on an iron plate and take it out on to the verandah or put it into a fume closet. Ignite the rag and hold a piece of white porcelain in the sooty flame.

The black, amorphous deposit is carbon. It is called "*lamp-black.*"

This specimen would contain a certain amount of oil. This oil can be removed by warming the lamp-black in a current of chlorine gas.

5. The charcoal produced by the dry distillation of bones is called "*animal charcoal.*" It possesses in a high degree the property of bleaching solutions which contain a small amount of colouring matter.

It is used commercially for decolorising sugar solutions. *Blood charcoal* possesses similar properties. Bleach the given coloured solution with the animal charcoal supplied.

6. The charcoal produced by the dry distillation of wood is called *wood charcoal.* It possesses in a high degree the power of adsorption. Repeat Expt. 28, page 29.

This principle may be adapted to the removal of noxious smells over drains, etc.

Expt. 67.—**Action of acids on carbon.**—Try the action of HCl, H_2SO_4, and HNO_3 on various forms of carbon.

Tabulate your results.

Expt. 68.—**Carbon is a reducing agent.**—Mix up some powdered black copper oxide with one-fifth its weight of powdered carbon and heat in a test-tube. Observe the reddish, metallic residue of copper. Carbon is a "*reducing agent.*"

$$\underset{\substack{\text{Cupric}\\ \text{oxide}}}{CuO} \quad \underset{\substack{\text{heated}\\ \text{with}}}{+} \quad \underset{\text{Carbon}}{C} \quad \underset{\text{gives}}{=} \quad \underset{\substack{\text{Metallic}\\ \text{copper}}}{Cu} \quad \underset{\text{and}}{+} \quad \underset{\substack{\text{Carbon}\\ \text{monoxide}}}{CO}$$

or,

$$\underset{\substack{\text{Cupric}\\ \text{oxide}}}{2CuO} \quad \underset{\substack{\text{heated}\\ \text{with}}}{+} \quad \underset{\text{Carbon}}{C} \quad \underset{\text{gives}}{=} \quad \underset{\substack{\text{Metallic}\\ \text{copper}}}{Cu} \quad \underset{\text{and}}{+} \quad \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{CO_2}$$

Test with lime-water.

Expt.—Find the percentage of incombustible ash in the given sample of coal.

Method—Demonstration 6, Expt. 30, page 31.

DEMONSTRATION 16

OXIDES OF CARBON

EXPT. 69.—**Carbonic acid gas. Carbon dioxide.**—Take a piece of carbon in a deflagrating spoon and heat it in the Bunsen flame until it glows. Now put it, still glowing, into a clean, dry gas cylinder and leave it there until it ceases to glow.

Shake up some ordinary air with lime-water—no effect will be observed.

Remove the deflagrating spoon from the cylinder and shake up the gas in the cylinder with lime-water. The lime-water will turn milky. What has happened ?

By the combustion of the carbon a new substance has been synthesised which possesses the property of turning lime-water milky. This substance is a compound of carbon and oxygen called carbon dioxide (di = two) or carbonic acid gas. Its formula is CO_2.

EXPT. 70.—**To prepare carbon dioxide gas in quantity.**—Take a Woulfe's bottle and fit it, as shown in Fig. 50, with a thistle funnel and delivery tube.

Into the bottle put some pieces of marble, or *any other cheap carbonate.* Fit in the corks and arrange the apparatus for the collection of the gas by the downward displacement of air. (See Fig. 50.)

Pour water in the Woulfe's bottle to a depth of about

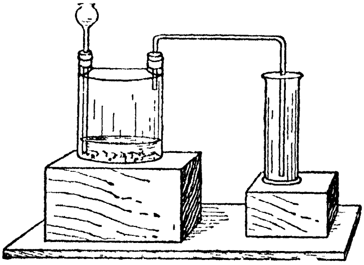


FIG. 50.

¾ inch. Place the gas jar so that the delivery tube dips to the bottom of the jar.

Through the thistle funnel pour in strong (commercial) hydrochloric acid.

Notice the brisk action that takes place, and that the liquid in the bottle gets warm. This rapid evolution of bubbles is called "effervescence."

The gas passes over through the delivery tube into the gas cylinder. The cylinder is shown to be full when a lighted match held at the mouth of the cylinder is extinguished.

Collect seven or eight jars of the gas.

Expt. 71.—**Test the properties of the gas.**—Write your results in tabular form.

(1) Notice its peculiar smell and that the gas has no colour. Taste the gas.

(2) Show that the gas is a non-supporter of combustion. Does it burn?

(3) Shake the gas with lime-water. What happens? (This constitutes a test for carbon dioxide gas.)

(4) Pour the gas from one vessel to another to show that it is heavier than air. (Test with lime-water.)

(5) Shake the gas with blue litmus solution. What do you observe and what conclusion do you come to?

(6) Test the solubility of the gas in water and the reaction to litmus of the water which has been shaken up with the gas.

(7) Bind a piece of magnesium ribbon to a deflagrating spoon. Heat the magnesium ribbon until it commences to burn. Plunge the burning ribbon into a cylinder of the carbon dioxide gas. Notice the flecks of carbon on the sides of the cylinder. A white substance will also be observed. Shake up the gas in the cylinder with litmus solution. Notice that the litmus indicates the presence of an alkali. The magnesium has taken the oxygen from the carbon dioxide and formed a basic oxide which is soluble in water.

CO_2	+	2Mg	=	C	+	2MgO
Carbon dioxide	with	(burning) Magnesium	yields	Carbon	and	Magnesium oxide

MgO	+	H_2O	=	$Mg(OH)_2$
Magnesium oxide	with	Water	gives	Magnesium hydroxide

The hydroxide gives the tests for the "OH" group. (See Demonstration 11, Expt. 54.)

EXPT. 72.—**Calcium bicarbonate.**—Take some lime-water in a test-tube and pass carbon dioxide gas through it. The lime water turns milky. This is due to the precipitation of calcium carbonate.

$Ca(OH)_2$	$+$	CO_2	$=$	$CaCO_3$	$+$	H_2O
Lime-water	and	Carbon dioxide	give	Calcium carbonate (white precipitate)	and	Water

If the carbon dioxide gas is passed into the solution in which the calcium carbonate is suspended the milky liquid becomes quite clear. This is due to the formation of a new compound of calcium called calcium bicarbonate.

$CaCO_3$	$+$	$H_2O + CO_2$	$\rightleftarrows$	$Ca(HCO_3)_2$
Calcium carbonate (insoluble)				Calcium bicarbonate (soluble)

Boil the clear solution. Carbon dioxide is evolved and calcium carbonate reprecipitated. The reversibility of the reaction is indicated by the reversed arrows $\rightleftarrows$.

Try the experiment with a solution of magnesium hydroxide in water and compare the results with those obtained with lime-water.

The temporary hardness of water (*vide* Demonstration 11) is due to the presence in the water of such salts as the bicarbonates of calcium and magnesium which are decomposed by boiling.

Use soap solution and repeat the experiments on hard and soft water (Demonstration 11).

Blow air from your lungs through lime-water. What happens? Why?

DEMONSTRATIONS

1. The demonstrator will show you that the air exhaled (breathed out) from your lungs contains more carbon dioxide than the air you inhale.

The apparatus is shown in Fig. 51.

The mouth is applied to a tube attached to *C*.

2. The apparatus used for showing the volumetric composition of carbon dioxide will be exhibited and its use explained.

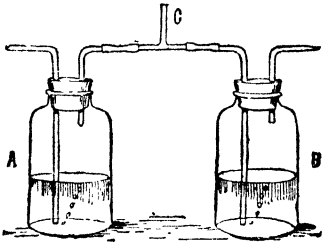


Fig. 51

Draw sketches of both these pieces of apparatus in your notebook and make notes on the method in which they are used.

Notes to Demonstrators

(1) Blackboard chalk is NOT a carbonate.

(2) The demonstrator is advised *not* to call carbon dioxide gas "chalk gas." It introduces to the mind of the student the idea that it is produced from chalk and chalk only.

Hence when, on some subsequent occasion, the student tests a gas produced by the action of a dilute acid on a solid and detects CO_2 he says that the substance from which he got the gas is "chalk." The fallacy of such an argument is obvious since ANY carbonate would give the gas, *not* chalk only.

This is dealt with further in the next demonstration.

DEMONSTRATION 17

CARBONATES AND BICARBONATES

When carbon dioxide gas is passed into a solution of an hydroxide a substance called a carbonate is formed. These bodies are substitution products of an acid called "carbonic acid"(H_2CO_3).

The "basicity" of an acid is the **number** of atoms of hydrogen in one molecule of the acid which are capable of being replaced by a metal (or a group of atoms equivalent to a metal).

Carbonic acid contains two atoms of replaceable hydrogen in each molecule, and is therefore **dibasic** (di=two).

A body formed from an acid by the replacement of a part or all of its hydrogen by a metal or its equivalent is called a **salt.**

Carbonic acid can give two series of compounds called salts.

(1) Those in which only one atom of hydrogen of the acid is replaced by a metal (or group of atoms equivalent to a metal= basic radical).

These are called **bicarbonates,** *e.g.*, $NaHCO_3$, sodium bicarbonate.

When only a portion of the replaceable hydrogen in an acid is replaced by a metal or its equivalent, the body so formed is called an "acid" salt. Sodium bicarbonate is an "acid" salt.

(2) Those in which all the replaceable hydrogen of the acid is replaced by a metal or its equivalent.

These are called **carbonates,** *e.g.*, Na_2CO_3 is called sodium carbonate or "normal" sodium carbonate.

The student must remember that it is not necessary that *all* the hydrogen in a molecule of an acid should be *capable* of replacement as it is in H_2SO_4, sulphuric acid, and H_2CO_3, carbonic acid. For example, in H_3PO_3, phosphorous acid, only two out of three atoms of hydrogen are capable of replacement. Therefore the acid is a *dibasic* acid and Na_2HPO_3 is the formula for *normal* sodium phosphite. Again, $C_2H_4O_2$ (or CH_3COOH), acetic acid, contains four atoms of hydrogen, but only one is capable of replacement by a metal or its equivalent. Therefore it is a **monobasic acid** (mono=one).

EXPT. 73A.—**Tests for carbonates.**—1. Nearly all carbonates on being heated dry give carbon dioxide gas and a residue of metallic oxide.

Exceptions: Barium carbonate and the carbonates of the alkali metals.

2. ALL carbonates when treated with DILUTE nitric acid give carbon dioxide gas with effervescence. Carbon dioxide gas turns lime-water milky. The gas is tested by pouring it into a test-tube containing a little clear lime-water. The student is warned against the common mistake of shaking some of the body to be tested into the lime-water and mistaking that, in a state of suspension, for the "milkiness."

Note also that this test only tells you that **a** *carbonate is present. It gives no hint as to* **what** *carbonate.*

N.B.—1. Be sure you use DILUTE acid.
2. Do not boil the reaction mixture so that acid fumes distil over into the lime-water.
3. Ask the demonstrator to show you how to "pour" the gas from one tube to another.

EXPT. 73B.—**Test for bicarbonates.**—If the given substance, when treated with dilute nitric acid, gives effervescence and carbon dioxide gas is evolved the substance must be a carbonate *or* a *bi*carbonate.

All bicarbonates are soluble.

Add a solution of magnesium sulphate to a solution of the given substance. If a white precipitate forms a *carbonate* is present. If no precipitate forms in the cold, but, on boiling, a white precipitate is thrown down, a *bicarbonate* is present.

EXPT. 73C.—Test each of the given bodies thus:

(1) Heat them dry. Is carbon dioxide evolved? Is any water vapour evolved? Describe the residue. Try the action of dilute hydrochloric acid on the residue.

(2) Treat with dilute nitric acid. Describe what happens. Is carbon dioxide evolved?

(3) Test their solubility in water. If soluble, test to see if the body is a normal carbonate or a bicarbonate.

Use small quantities.

Tabulate your results.

Sub-stance.	I heated the substance dry in a test-tube.			Action of dilute hydrochloric acid or dilute nitric acid.	Is the sub-stance soluble ?	Car-bonate or bicar-bonate ?
	Is CO_2 evolved ?	Is water vapour given off ?	Describe the changes which take place.			
A						
B						
C						

Ask the demonstrator to examine your results at once if you are in any doubt.

Sodium Carbonate

Sodium carbonate is a most important carbonate.

Expt. 74.—(1) You are given some crystals of " washing soda." Examine them carefully. Describe them and select a good specimen and make a sketch of it.

(2) Show that water is given off when sodium carbonate crystals are heated in a test-tube. Collect the water in a second tube. Heat the tube containing the crystals carefully or you will break the tube. (See Fig. 52.)

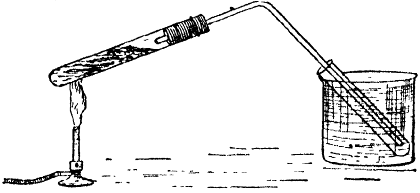


Fig. 52.

(3) Leave some of the crystals exposed to atmosphere in the laboratory. They should effloresce (*vide* Expt. 22, page 28).

(4) Dissolve some of the crystals in water. Test the action of the solution to litmus solution. (See Demonstration 26, page 112.)

(5) Dissolve 10 grams of anhydrous sodium carbonate in 20 c.c.

of water. To the solution add milk of lime, made by shaking up 200 grams of slaked lime with 250 c.c. of water. Boil in an iron pan for some time. Remove the burner and allow the mixture to stand. Carefully pour off the clear upper layer. Evaporate it down to a quarter of its former bulk in an iron pan. Cool the solution and then feel it by dipping the fingers into it and then rubbing them together. Do you notice the "slimy" or "soapy" feeling? It is due to the caustic alkali, sodium hydrate (NaOH). A "caustic" substance is one that burns the skin.

The action which takes place is expressed by the equation:

Na_2CO_3	+	$Ca(OH)_2$	=	$2NaOH$	+	$CaCO_3$
Sodium carbonate	with	Calcium hydrate	gives	Caustic soda (sodium hydrate)	and	Calcium carbonate

To this solution apply the tests for the hydroxyl group or hydroxides given in Expt. 54, page 57. An iron vessel is used for the experiment, as glass or porcelain would be attacked by the caustic alkali.

EXPT. 75.—**Find the loss per cent. in the weight of the given substance when heated.**—Weigh a clean crucible. In it put about 1 to 2 grams of the substance and weigh again. Put the crucible on a clay triangle and heat with the Bunsen flame until the weight is constant. Remember to let the last part of cooling take place in a desiccator. Never weigh a hot crucible. Use the tongs provided.

Data:—

Weight of the empty crucible and lid = W grams.
Weight of crucible, lid and substance = w ,,
Weight of substance taken = $(w-W)$,,
Weight of crucible, lid and residue = w_1 ,,
Loss of weight = $(w-w_1)$,,

Required percentage loss will be:

$$\frac{(w-w_1)}{(w-W)} \times 100 \quad . \; . \; . \; . \; . \; . \; . \quad \textit{Ans.}$$

DEMONSTRATION 18

EXPT. 76.—**Determination of the percentage loss in weight sustained by a carbonate when treated with a dilute acid.**—Take a small flask with a short wide neck and fit it with a good cork. Take a glass tube and bore a hole in the cork which will fit the tube.

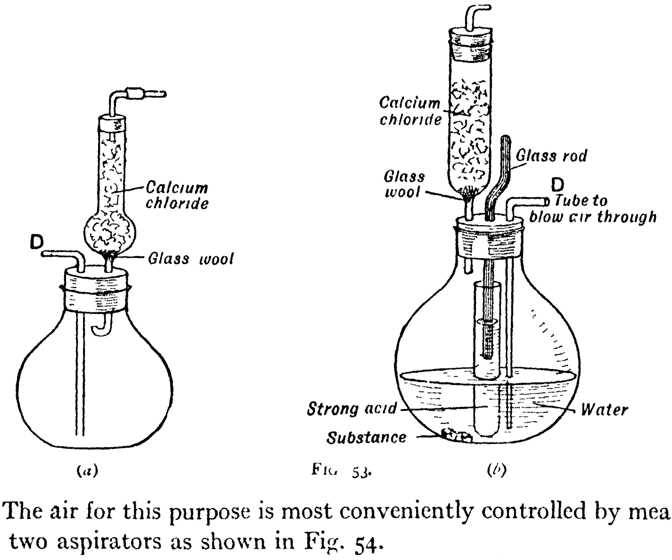
Fill a small calcium chloride tube with fused calcium chloride and fit it in the cork also, so that the apparatus shown in Fig. 53 (*a*) is fitted up. Do not forget to round off all glass tubes before passing them through the cork. Fit the wide end of the calcium chloride tube with a cork through which is passed a short bent tube. When not in use the free end of the calcium chloride tube should be closed with a stop made of a piece of rubber tubing one end of which is closed with a short length of glass rod. This stop should be removed when weighing the apparatus.

See that the apparatus is air-tight.

Weigh the apparatus. Add about a gram of the carbonate and weigh again. The difference in the first and second weighings gives the weight of the carbonate taken. Add about 30 c.c. of distilled water. Select a small test-tube which will just go in the bulb of the flask, and three-quarters fill it with strong hydrochloric acid. Slide the test-tube into the flask and it will rest slanting against the wall of the flask. Replace the cork and weigh the whole apparatus.

Remove the apparatus from the balance and leave the balance and weights in order.

Now tilt the apparatus and the concentrated hydrochloric acid will mix with the water and act upon the carbonate, giving carbon dioxide, which, in escaping through the calcium chloride, will be completely dried. When all action has subsided slightly warm the bottle by putting it in warm water, and blow dry air through the side tube *D* (Fig. 53 (*b*)). This process is adopted to drive any carbon dioxide out of solution and to replace the carbon dioxide in the apparatus by air. Cool the flask in tap-water. Wash, dry, and weigh again.



(*a*) FIG. 53. (*b*)

The air for this purpose is most conveniently controlled by means of two aspirators as shown in Fig. 54.

B is full of water, *A* is full of air. By opening the pinch-cock between *A* and *B* the air from *A* is driven out. It is dried by passing it through a Woulfe's bottle containing sulphuric acid. The pace at which the air is flowing can be seen by the rate at which the bubbles come through the sulphuric acid. When the water has run out of *B* connect the drying bottle to the glass tube in the stopper of *B*; place *B* on the table and put *A* on a wooden block.

Data :

Weight of the bottle empty = m grams.
Weight of bottle and carbonate = m' ,,
∴ Weight of carbonate taken = $(m'-m)$,,

Data:

Weight of complete apparatus, carbonate, acid, etc. = a grams.
Weight of complete apparatus after the experiment = b „
∴ Weight of carbon dioxide evolved = $(a-b)$ „
Loss of weight sustained by $(m'-m)$ grams of carbonate = $(a-b)$ „
∴ Loss of weight sustained by 1 gram of carbonate = $\frac{(a-b)}{(m'-m)}$ „
∴ Loss of weight sustained by 100 grams of carbonate = $\frac{(a-b)}{(m'-m)} \times 100$ „
∴ *Required loss per cent. is . . . . per cent. Ans.*

The student may find it difficult to prevent the test-tube containing strong acid from upsetting before it is required to do so. This upsetting may be prevented by passing a piece of thin glass rod through the cork (Fig. 53 (a)). Put the tube containing strong acid in the flask and then, holding the flask in a slightly slanting position, but taking care that the acid does not upset, carefully insert the cork in such a way that the glass rod runs into the test-tube. The flask may now be raised to the vertical position without any risk of the tube upsetting. When the weighing is completed pull up the glass rod and spill the acid.

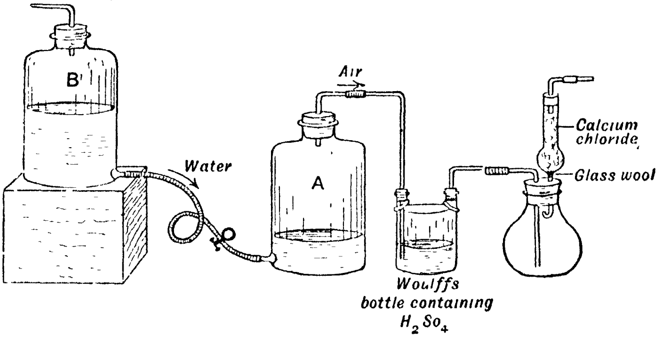


FIG. 54

DEMONSTRATION 19

EXPT. 77.—**To find the percentage of carbonate in a mixture the other constituents of which are unaffected by dilute hydrochloric acid.**—The procedure is exactly the same as in the previous experiment, but the calculation is worked out as follows :—

Suppose the carbonate is magnesium carbonate.

Data :

Weight of the empty bottle = m grams.
Weight of bottle and mixture = m' ,,
∴ Weight of the mixture taken = $(m'-m)$,,
Weight of complete apparatus with substance, acid, etc. = a ,,
Weight of complete apparatus after experiment = b ,,
∴ Loss of weight (CO_2 evolved) = $(a-b)$,,

Now the molecular weight of magnesium carbonate, $MgCO_3$, is $(24+12+48)=84$, and the quantity of carbon dioxide contained in it is 44 parts.

∴ 44 grams of CO_2 would be evolved from 84 grams of $MgCO_3$.

i.e., 1 gram of CO_2 would be evolved from $\frac{84}{44}$ grams of $MgCO_3$.

∴ $(a-b)$ gram of CO_2 would be evolved from $\frac{84}{44}\times(a-b)$ grams of $MgCO_3$.

i.e., the amount of $MgCO_3$ in $(m'-m)$ grams of mixture is $\frac{84}{44}\times(a-b)$ grams.

∴ the amount of $MgCO_3$ in 1 gram of mixture is $\frac{84}{44}\times\frac{(a-b)}{(m'-m)}$ grams.

∴ the amount of $MgCO_3$ in 100 grams of mixture is $\frac{84}{44}\times\frac{(a-b)}{(m'-m)}\times 100$ grams.

∴ *Required percentage of carbonate is . . . per cent.* ***Ans.***

DEMONSTRATION 20

CARBON MONOXIDE. OXALATES

Perform your experiments in a fume closet, as carbon monoxide is very poisonous.

EXPT. 78.—**Preparation of carbon monoxide.**—Fit up the apparatus shown in Fig. 55. Do not forget to round off all the tubes before pushing them through corks or into rubber tubing.

Be sure all parts of your apparatus are air-tight.

A boiling tube, *A*, is fitted with a cork. Through this is passed a glass delivery tube which in turn passes into a bottle or flask, *B*. The delivery tube from the wash-bottle, *B*, is conducted under a test-tube, *C*, or small cylinder filled with water and inverted in a trough of water.

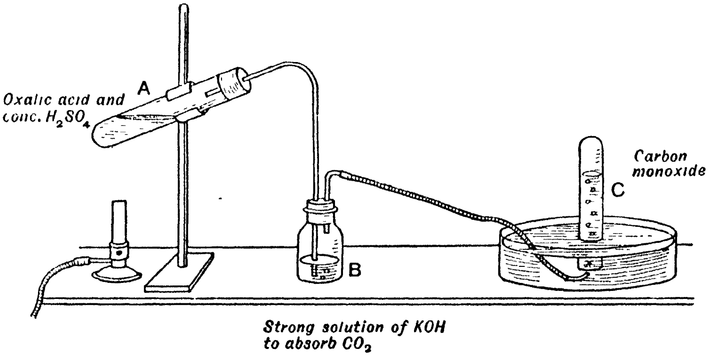

Oxalic acid and conc. H_2SO_4
A
Carbon monoxide
C
B
Strong solution of KOH to absorb CO_2

FIG 55.

Into the boiling tube put some crystals of oxalic acid and upon them pour concentrated sulphuric acid. Fit the tube in the stand and push its cork tightly in its mouth.

Put some crude caustic potash or caustic soda solution in the wash-bottle, *B*. (The "crude" chemical is used because it is as efficient as, and cheaper than, the pure chemical.)

Gently warm the boiling tube. Gas comes off, but notice that there is no blackening in the tube. The first one or two tubes of gas will be impure, as they will contain air which has been swept out of the apparatus.

$$\begin{array}{ccccccc} \begin{array}{c}\mathrm{COOH}\\ | \\ \mathrm{COOH}\end{array} & = & \mathrm{CO} & + & \mathrm{CO_2} & + & \mathrm{H_2O} \\ \text{Oxalic acid} & \text{yields} & \begin{array}{c}\text{Carbon}\\ \text{monoxide}\end{array} & \text{and} & \begin{array}{c}\text{Carbon}\\ \text{dioxide}\end{array} & \text{and} & \text{Water} \end{array}$$

The water remains behind in the test-tube with the strong sulphuric acid. The carbon dioxide is absorbed in the caustic potash.

$$\mathrm{KOH + CO_2 = KHCO_3}\ \text{(potassium bicarbonate).}$$
$$\mathrm{2KOH + CO_2 = K_2CO_3 + H_2O.}$$

EXPT. 79.—**Examine the properties of carbon monoxide.**

(1) The gas is colourless.

(2) It has a sweet smell, *but do not inhale it. It is very poisonous.*

(3) It is insoluble in water.

(4) Shake up with red and blue litmus solutions. The gas is neutral.

(5) Shake up with lime-water. It has no action. If the gas has not been properly "scrubbed" in the bottle *B*, it may give some milkiness with lime-water.

(6) Plunge a burning taper into a cylinder of the gas. The taper is extinguished. The gas burns with a pretty blue flame.

(7) Ignite a test-tube full of the gas and let it burn away. Pour in lime-water and shake up. The lime-water is turned milky because carbon dioxide is present.

$$\begin{array}{ccccc} \mathrm{2CO} & + & \mathrm{O_2} & = & \mathrm{2CO_2} \\ \begin{array}{c}\text{Carbon}\\ \text{monoxide}\end{array} & \begin{array}{c}\text{combines}\\ \text{with}\end{array} & \text{Oxygen} & \text{giving} & \begin{array}{c}\text{Carbon}\\ \text{dioxide}\end{array} \end{array}$$

EXPT. 80.—**Action of heat on oxalates.**—You are given specimens of oxalates. Heat them and *describe all that happens.*

Test the gases given off and write up your results in tabular form.

Effect of heat on oxalates.

Substance.	CO evolved	CO_2 evolved.	H_2O evolved	Remarks on changes during heating Describe Residue.
Sodium oxalate ..	Yes	No	Yes	Substance does not blacken white residue, which appears to be sodium carbonate, as with a dilute acid it effervesces, giving CO_2 (tested with lime-water).
Potassium binoxalate				
Ferrous oxalate ..				
Ammonium oxalate				
Lead oxalate				

Expt. 81.—**Effect of strong sulphuric acid on oxalates.**—Notice that they do not blacken.

Tabulate your results.

Expt. 82.—**Action of strong sulphuric acid on potassium ferrocyanide.**—Show that when strong sulphuric acid acts upon potassium ferrocyanide, carbon monoxide is formed. *Use small quantities.*

$$\underset{\text{Potassium ferrocyanide}}{K_4Fe(CN)_6} + \underset{\text{Water}}{6H_2O} + \underset{\text{Sulphuric acid}}{6H_2SO_4} \underset{\text{give}}{=} \underset{\text{Potassium sulphate}}{2K_2SO_4} + \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Ammonium sulphate}}{3(NH_4)_2SO_4} + \underset{\text{Carbon monoxide}}{6CO}$$

EXPT. 83.—**Action of strong sulphuric acid on formic acid.**—Formic acid is decomposed by sulphuric acid giving carbon monoxide.

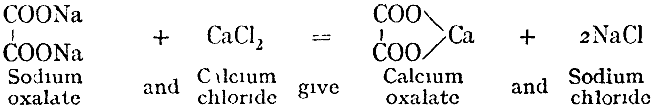
$$\underset{\text{Formic acid}}{H\cdot COOH} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Water}}{H_2O} + \underset{\text{Carbon monoxide}}{CO} + \underset{\text{Sulphuric acid}}{H_2SO_4}$$

EXPT. 84.—**Tests for oxalates.**—(1) Oxalates on being heated alone give either carbon monoxide and a residue of carbonate *or* carbon dioxide and carbon monoxide gases and a residue of oxide. Silver oxalate explodes and leaves metallic silver.

(2) With strong sulphuric acid oxalates give carbon dioxide and carbon monoxide. They do *not* blacken.

(3) In solution. Neutral solutions give a white precipitate of calcium oxalate soluble in dilute nitric or dilute hydrochloric acid.

Calcium oxalate is insoluble in acetic or oxalic acid.



$$\underset{\text{Sodium oxalate}}{\begin{matrix}COONa\\|\\COONa\end{matrix}} \underset{\text{and}}{+} \underset{\text{Calcium chloride}}{CaCl_2} \underset{\text{give}}{=} \underset{\text{Calcium oxalate}}{\begin{matrix}COO\\|\\COO\end{matrix}\!\!>Ca} \underset{\text{and}}{+} \underset{\text{Sodium chloride}}{2NaCl}$$

(4) Mix a solution of an oxalate with a solution of potassium permanganate and dilute sulphuric acid. What do you observe? What is the gas given off? Write equations representing the changes which take place.

To detect carbon monoxide in the presence of carbon dioxide use the apparatus shown above (Fig. 55). In the bottle, *B,* put lime-water. This shows whether or not carbon dioxide is present.

If the issuing gas burns with a blue flame and gives carbon dioxide, it is carbon monoxide.

DEMONSTRATIONS

(1) Preparation of carbon monoxide by passing carbon dioxide over red-hot carbon heated in an iron tube in a furnace.

The gas is collected over potassium hydroxide so that no carbon dioxide may pass over. The CO_2 is passed through strong H_2SO_4 to dry it (Fig. 56).

Draw sketch of the apparatus in your note-book.

Notice that in this case carbon dioxide is acting as an *oxidising* agent; it oxidises carbon, thereby becoming reduced carbon monoxide. Carbon is *reducing* carbon dioxide.

$$CO_2 + C = 2CO.$$

(2) The reducing action of carbon monoxide will be demonstrated.

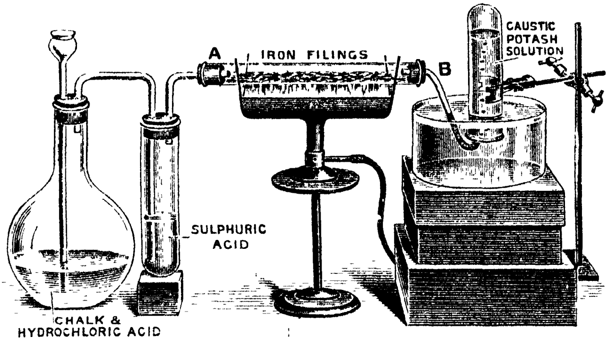


FIG. 56.

Hot copper oxide is reduced to the state of metallic copper by the action of carbon monoxide.

CuO	+	CO	=	CO_2	+	Cu
Copper oxide	and	Carbon monoxide	give	Carbon dioxide	and	Copper

(3) Carbon monoxide is soluble in a solution of cuprous chloride in strong hydrochloric acid (distinction from acetylene). The carbon monoxide forms a compound with cuprous chloride ($2CuCl,CO,2H_2O$). This compound is decomposed when heated with potassium hydrate solution.

DEMONSTRATION 21

Modes of Chemical Action

The different ways in which chemical action may take place may be roughly divided into five classes :—

(1) Direct union or synthesis.
(2) Displacement.
(3) Double decomposition.
(4) Direct decomposition.
(5) Internal rearrangement of atoms.

In this demonstration typical examples of each method will be studied.

I. **Direct union or synthesis.**—Expt. 85.—(*a*) *A* is a mixture of iron filings and sulphur.

Treat a little of the mixture with dilute hydrochloric acid. Notice the smell and properties of the gas evolved.

(*b*) Heat a little of the mixture in a small test-tube. Notice that, when the action in the tube has commenced as a result of heating the tube, it will continue without further heating. The mixture in the tube glows. Chemical action is taking place with the evolution of light and heat. Let the tube cool. Notice the difference in the appearance of its contents. Break the tube and treat the fragments with dilute hydrochloric acid. Observe the smell of the gas. Is it the same odour that was observed when the unheated mixture was treated with dilute hydrochloric acid? This gas is sulphuretted hydrogen (H_2S), produced by the action of dilute hydrochloric acid on ferrous sulphide (FeS). The ferrous sulphide has been synthesised by the action of iron on sulphur.

Fe	$+$	S	$=$	FeS
Iron	heated with	Sulphur	gives	Ferrous sulphide

FeS	$+$	$2HCl$	$=$	$FeCl_2$	$+$	H_2S
Ferrous sulphide	and	Hydrochloric acid	give	Ferrous chloride	and	Sulphuretted hydrogen

II. **Displacement.**—In this method of chemical change one element takes the place of another element in a compound.

Expt. 86.—*B* is a solution of copper sulphate ($CuSO_4$). The white metal *C* is zinc (Zn). Shake up some of the solution *B* with *C and be careful.* Shake gently or you will knock the bottom out of the test-tube. The blue solution gradually becomes quite clear and colourless, while, at the bottom of the tube, a red precipitate of metallic copper (Cu) is seen.

Zn	$+$	$CuSO_4$	$=$	$ZnSO_4$	$+$	Cu
Zinc	with	Copper sulphate	gives	Zinc sulphate	and	Copper

III. **Double decomposition.**—All reactions of the type represented by the equation $Ax + By = Ay + Bx$ are called double decompositions.

Expt. 87.—*D* is a solution of sodium carbonate.
E is a solution of strontium chloride.

What we wish to show is that if these solutions are mixed, sodium chloride and strontium carbonate will be formed by double decomposition.

We have already learned the tests for carbonates (Expt. 73A, page 80) and chlorides (Expt. 59, page 63).

Test for sodium.—When a platinum wire is dipped into a sodium salt and then heated in a clear Bunsen flame, the flame assumes a brilliant golden colour. *This is shown by every sodium compound without exception.*

Test for strontium.—When a platinum wire is dipped into a strontium salt and heated in a clear Bunsen flame a brilliant crimson flame is developed. *This is peculiar to strontium salts.*

We have now sufficient knowledge to test for *A*, *B*, *x* and *y* in the typical equation.

1. (*a*) To a little of *D* add dilute hydrochloric acid. CO_2 is evolved. Apply the lime-water test. The lime-water turns milky,

Therefore a CARBONATE *is present.*

(*b*) To the solution *D* add dilute nitric acid and warm until all the carbon dioxide has been evolved. To this solution add silver nitrate solution. No precipitate is formed.

Therefore a CHLORIDE *is not present.*

(*c*) Dip a platinum wire into *D* and put it in the clear Bunsen flame. A brilliant golden-coloured flame is produced.

Therefore SODIUM *is present.*

In the solution D, SODIUM *and* CARBONATE *are found.*

2. (*a*) To a little of the solution *E* add dilute nitric acid. There is no effervescence. No gas is evolved even on warming.

Therefore a CARBONATE *is not present.*

(*b*) To this solution add a solution of silver nitrate. A white precipitate is formed. It is soluble in ammonia, and reprecipitated by nitric acid.

Therefore a CHLORIDE *is present.*

(*c*) Dip a clean platinum wire in *E* and put it in a clear Bunsen flame. A brilliant crimson-coloured flame is produced.

Therefore STRONTIUM *is present.*

In solution E STRONTIUM *and* CHLORIDE *are found.*

3. **Now mix 20 c.c. of *D* with 20 c.c. of *E*.** A white precipitate is formed. Filter. Wash the precipitate carefully. (*a*) Take the precipitate and to it add dilute hydrochloric acid. Effervescence takes place. The gas given off turns lime-water milky. It is carbon dioxide.

Therefore the precipitate is a CARBONATE.

(*b*) Test the precipitate on a platinum wire in the Bunsen flame. A brilliant crimson-coloured flame is produced.

Therefore STRONTIUM *is present,*

i.e., the strontium which previously existed as strontium chloride has now been converted into strontium carbonate.

4. Test the filtrate for *chloride, carbonate, sodium* and strontium; of these the first three will be found to be present because sodium carbonate was added in excess.

All the strontium will be on the filter paper as strontium carbonate and therefore strontium will not be found in the filtrate.

The reaction which you have just investigated is represented by the equation:

Na_2CO_3	$+$	$SrCl_2$	$=$	$SrCO_3$	$+$	$2NaCl$
Sodium carbonate	with	Strontium chloride	gives	Strontium carbonate	and	Sodium carbonate

IV. **Direct decomposition.**—Expt. 88.—Heat mercuric oxide, *F*, in a test-tube. Test the gas given off and show that it is oxygen (Expt. 40, page 43). Observe the mirror formed on the upper part of the tube. Rub the mirror with a rod and note the globules are formed. *Mercury is the only metal which forms globules under these conditions.*

$2HgO$	$=$	$2Hg$	$+$	O_2
Mercuric oxide	decomposes into	Mercury	and	Oxygen

V. **Internal rearrangement of atoms in a molecule.**—There are many examples of this form of chemical change, but they mostly belong to the province of Organic Chemistry (*i.e.*, the Chemistry of the Carbon Compounds), and for the present are beyond the scope of the student.

An example from Inorganic Chemistry is given here.

Expt. 89.—Take some of the solution *G* and notice its colour. Warm it carefully and observe what happens. Above 80° C. the colour of the solution changes to green. Cool the tube under the tap. It should recover its violet colour, but the change may be delayed. This change in colour is probably due to the rearrangement of the atoms in the dissolved molecules.

DEMONSTRATION

The growth of a " lead tree " and a " silver tree " will be shown to you. **Do not disturb the vessels** in which the experiments are being performed.

Notes to Demonstrators

Expt. 87. Arrange the strength of *D* and *E* so that 20 c.c. of *D* will contain more than sufficient sodium carbonate to precipitate the strontium in *E*. Use *pure* chemicals.

Expt. 89. The solution *G* is violet chromium chloride or sulphate.

Demonstrations.—(1) Hang up zinc in lead acetate solution.
(2) Hang up zinc in silver nitrate solution.

DEMONSTRATION 22

Conditions Affecting Chemical Change

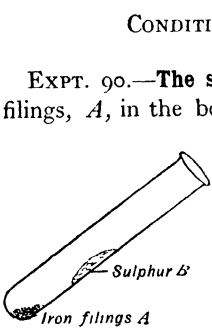


FIG. 57.

EXPT. 90.—**The substances must be in contact.**—Put some iron filings, *A*, in the bottom of a test-tube. Holding the tube in a slanting position and using a spatula, put some powdered sulphur, *B*, in the tube about one-third the length of the tube from the bottom (see Fig. 57). Now commence heating the tube from the bottom. Heat both the iron and the sulphur. Nothing happens until the sulphur melts and runs down the wall of the tube and comes into contact with the iron filings. Chemical action takes place with the evolution of light and heat. Iron sulphide is formed.

Fe	$+$	S	$=$	FeS
Iron filings	and	Sulphur	combine to form	Iron (ferrous) sulphide

EXPT. 91.—**Influence of water.** (*a*) **Chemical action can proceed as a result of the substances being in solution.**—Take some substance (*C*) and mix it with some of *D*. Nothing happens. Add water to the mixture. At once a brisk effervescence ensues and carbon dioxide gas is evolved (apply lime-water test).

Water was necessary for the action to proceed.

C is oxalic acid. *D* is sodium carbonate.

$H_2C_2O_4$	$+$	Na_2CO_3	$=$	$Na_2C_2O_4$	$+$	CO_2	$+$	H_2O
Oxalic acid	and	Sodium carbonate	give	Sodium oxalate	and	Carbon dioxide	and	Water

(*b*) **In some cases traces of water are sufficient to cause a chemical action to proceed.**—The cylinder labelled *E* contains dry sulphur dioxide gas.

The cylinder labelled *F* contains dry sulphuretted hydrogen gas.

Expt. 91a.—**Water as a catalyst.**—Invert the cylinders over each other so that the cover glasses are in contact. Hold the cylinders steady and slip the cover glasses away carefully but quickly. The gases will mix by diffusion (Expt. 27, page 29), but no change can be observed. Blow two or three drops of water into the cylinders by means of a pipette. Shake up. A white deposit of sulphur will appear on the walls of the cylinders, showing that chemical action has taken place.

The reaction may be roughly represented by the equation :

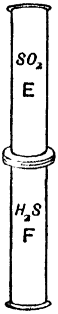


Fig. 58.

SO_2	$+$	$2H_2S$	$=$	$3S$	$+$	H_2O
Sulphur dioxide	and	Sulphuretted hydrogen	react, giving	Sulphur	and	Water

Expt. 92.—**Influence of temperature.**—Observe the action of heat on *G* (mercuric oxide), *H* (potassium chlorate), *J* (mixture of iron filings and sulphur), and *K* (ammonium dichromate). The action of heat on *G, H,* and *J* has been fully explained in previous demonstrations. *K* is given to you as a striking experiment. The substance is outside your syllabus.

Expt. 93.—**Influence of light.**—(*a*) Expose a piece of photographic printing-out paper (*L*) to the influence of direct sunlight.

Observe that it passes through various shades of yellow and brown until it finally becomes nearly black. Chemical action is taking place on the surface of the paper as a result of the influence of light.

(*b*) Add silver nitrate solution to a solution of sodium chloride. A white precipitate is formed :

$AgNO_3$	$+$	$NaCl$	$=$	$AgCl$	$+$	$NaNO_3$
Silver nitrate		Sodium chloride		Silver chloride (white precipitate)		Sodium nitrate

Put the tube in the sunlight. The precipitate turns violet in colour. Test the filtrate with a solution of potassium iodide mixed with starch solution. The solution should turn a blue colour, showing the presence of free iodine released from the potassium iodide by the chlorine given out by the action of light on silver chloride.

EXPT. 94.—**Catalytic agents.**—(*a*) Try the action of heat on potassium chlorate alone. Then mix a little manganese dioxide with some potassium chlorate and heat it. It will be found easier to obtain oxygen from the chlorate when it is mixed with manganese dioxide than when there is no manganese dioxide present. The manganese dioxide is unchanged in the reaction.

Perform tests to ascertain whether other substances such as powdered glass will accelerate the decomposition of potassium chlorate when it is heated.

(*b*) Treat the given solution of hydrogen peroxide with (i) powdered copper, (ii) powdered glass. What happens?

Perform tests on the copper and glass before and after the experiment to ascertain if any change has taken place in them.

(*c*) The manufacture of chlorine by Deacon's process will again be demonstrated to you (see page 70).

Those bodies which assist a chemical action to proceed in a desired direction without themselves being changed at the end of the reaction are called **catalytic agents.**

The phenomenon is called **catalysis.**

EXPT. 95.—**Removal of the products of reaction. Mass action.**—Take 10 c.c. of cold concentrated hydrochloric acid and to it add small quantities of M (red antimony sulphide) until no more of M will dissolve in the cold acid. Allow the excess of M to settle down and then pour off the clear solution into a test-tube. Divide the clear solution into two portions, α and β. Boil α, but do not boil β. After heating α, to both α and β add an excess of cold water. The solution α gives a white precipitate (antimony oxychloride) and the solution β gives an orange-red precipitate (antimony sulphide).

Explanation.—M is soluble in strong cold hydrochloric, but it is not soluble in cold dilute hydrochloric acid. When M is dissolved in cold concentrated hydrochloric acid the reaction which takes place is represented by the equation :

$$\underset{\substack{\text{Antimony}\\ \text{trisulphide}}}{Sb_2S_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{6HCl} \rightleftharpoons \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen}}}{3H_2S} + \underset{\substack{\text{Antimony}\\ \text{trichloride}}}{2SbCl_3}$$

The solution—a mixture of sulphuretted hydrogen, antimony trichloride, and hydrochloric acid in water—is divided into two parts, α and β. (i) If the solution α is boiled the sulphuretted hydrogen is driven off and removed from the sphere of action (in this case the sphere of action is the solution) and you are left with a solution of antimony trichloride and hydrochloric acid in water. On dilution with water the concentration of the hydrochloric acid is lowered and a white precipitate of antimony oxychloride is formed.

$$\underset{\substack{\text{Antimony}\\ \text{trichloride}}}{SbCl_3} \underset{\text{in}}{+} \underset{\substack{\text{dilution}\\ \text{with water}}}{H_2O} \underset{\text{gives}}{\rightleftharpoons} \underset{\substack{\text{Antimony}\\ \text{oxychloride}}}{SbOCl} \underset{\text{and}}{+} \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{2HCl}$$

(ii) On the other hand, if the unboiled portion, β, is diluted the concentration of the hydrochloric acid is lowered (*i.e.*, the hydrochloric acid becomes dilute) and the point arrives at which the antimony trisulphide is insoluble in the dilute hydrochloric acid, therefore, on adding water we get an orange-red precipitate of antimony trisulphide (Sb_2S_3).

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl$$

This reaction has now been shown to be a reversible one and the direction which it takes will depend upon the " concentration " of the hydrochloric acid present.

$$\text{"Concentration"} = \text{mass of solute per unit volume of solution.}$$
$$= \frac{\text{mass of hydrochloric acid in solution.}}{\text{volume of hydrochloric acid solution.}}$$

This " concentration " is lowered when water is added to the strong hydrochloric acid solution because the volume of the solution increases while the mass of hydrochloric acid present remains constant.

Hence the antimony sulphide can be formed in the dilute solution produced, and its formation or non-formation by the action of sulphuretted hydrogen on antimony trichloride depends entirely on the concentration of the hydrochloric acid present.

The influence, which depends entirely on the concentration of one or more of the substances taking part in a chemical reaction, is called the influence of mass or **mass action.**

N.B.—If preferred this experiment may be performed as a "Demonstration" and the theory very carefully explained.

Expt. 96.—**Electricity.**—The demonstrator will show you the analysis (splitting up) of hydrochloric acid by means of electricity in a Hoffmann's Voltameter. Note that carbon electrodes are used because the free chlorine which is evolved in the reaction would attack metallic electrodes.

Expt. 97.—**Percussion.**—The demonstrator will explode a small quantity of a body by placing it on a small steel anvil and hitting it with a hammer.

DEMONSTRATION 23

Expt. 98.—**To determine the percentage gain (or loss) in weight when *A* is heated with an excess of *B*.**—Clean the porcelain crucible supplied. Heat it on the clear Bunsen flame and allow it to finish cooling off in a desiccator. Always lift the crucible with the tongs.

Weigh the crucible (W). Now weigh out, in a weighing tube, one to one and a half grams of the substance A (w). Take a glazed mortar and, placing it on a piece of black glazed paper, put into the mortar about six or seven grams of the substance B. Turn the substance A into the mortar. The tube must now be weighed again (w_1). Thoroughly mix the two substances in the mortar by means of a glazed pestle. Keep the mortar on the glazed paper all the time, so that if, in the process of mixing, any of the substance is spilt, it is not lost.

Put your weighed crucible on the glazed paper, put a little of B in the bottom of it. Now turn the mixture of A and B in the mortar into the crucible. Put a little of B into the mortar. Rub it round with the pestle and put it in the crucible also. Repeat this and the pestle and mortar may be considered clean from the weighed substance A. Put any particles of the substance which got spilled on the glazed paper in the crucible also.

The crucible may be set on a pipe-clay triangle and heated gently at first, afterwards more strongly (see Fig. 35, page 38). Cool, weigh. Repeat the heating until the weight is constant. Remember not to handle the crucible with the fingers. Always use the tongs provided. If fumes are given off the crucible should be heated in a fume closet or under a hood.

Data :

Weight of crucible = W grams.
Weight of weighing tube and substance A = w ,,
Weight of weighing tube and residue = w_1 ,,
Weight of A taken = $(w-w_1)$,,
Weight of crucible when weight is constant after heating = w_2 ,,
Weight of substance formed = (w_2-W) ,,

(Suppose the substance gains in weight).

Gain in weight of $(w-w_1)$ grams of $A=(w_2-W)-(w-w_1)$ grams.

$\therefore$ Gain in weight of 1 gram of A $=\dfrac{(w_2-W)-(w-w_1)}{(w-w_1)}$,,

$\therefore$ Gain in weight of 100 grams of A =

$$\frac{\{(w_2-W)-(w-w_1)\}}{(w-w_1)}\times 100 \text{ grams.}$$

Required percentage gain in weight = . . . *Ans.*

Note to Demonstrators

In order that this experiment may be carried out quantitatively it is essential that B should be a VOLATILE substance.

Examples of suitable substances are :

A = Barium peroxide, B ammonium chloride.
A = Calcium oxide, B ammonium sulphate.
A = Magnesia, B ammonium sulphate.

With slight modifications in procedure the following may be employed :

A = Sodium sulphite, hypo, potassium chloride, etc.
B = Sulphuric acid.

DEMONSTRATION 24

PREPARATION AND PROPERTIES OF NITRIC ACID. TESTS FOR NITROUS AND NITRIC ACIDS. CHEMICAL ACTION OF NITRIC ACID

EXPT. 99.—**Preparation of nitric acid.**—Take a 250 c.c. retort and put in it some sodium nitrate (Chili saltpetre, $NaNO_3$). Fit it in a sand-bath on a retort stand. Arrange the apparatus as shown in Fig. 59. The neck of the retort is slipped into the neck of a flask which is lying slantwise in a trough of cold water. Pack the mouth of the flask with a little glass wool. Wet a piece of filter paper and lay it over the flask where it protrudes above the surface of the water in the trough. Pour concentrated sulphuric acid into the retort by means of a glass funnel inserted through the tubulure. Replace the stopper. If it is not air-tight grease the stopper with high melting-point wax. Heat the retort slowly, gradually increasing the temperature as the reaction proceeds. Keep the receiver cool by pouring cold water from the trough over the filter paper. Describe carefully all you do and see, etc. When

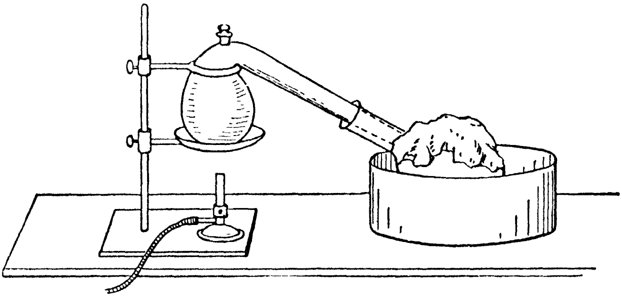


FIG. 59.

the reaction is finished remove the flask and pour the contents of the retort into an evaporating basin and set aside to cool. Crystals of sodium bisulphate separate out. Pour the liquid off from the crystals. Dissolve the crystals in water. Evaporate down the solution and set aside to crystallise again.

The reaction which has taken place is represented by the equation :

$$\underset{\text{Sodium nitrate}}{NaNO_3} \underset{\text{and}}{+} \underset{\text{strong Sulphuric acid}}{H_2SO_4} \underset{\text{give}}{=} \underset{\text{Sodium bisulphate}}{NaHSO_4} \underset{\text{and}}{+} \underset{\text{Nitric acid}}{HNO_3}$$

The liquid in the flask is nitric acid. Be careful not to get the acid on your fingers.

Tabulate your results.

EXPT. 100.—**Properties of nitric acid.**—(*a*) Smell the liquid and note its unpleasant and characteristic odour.

(*b*) Put two drops of acid in a test-tube, fill the tube up with water and taste the solution.

(*c*) Test the action of the solution (*b*) with litmus paper or solution.

(*d*) Dilute a sample of the strong acid with four times its volume of water and test its action with

(i) Calcium carbonate.
(ii) Metallic magnesium.
(iii) Caustic soda solution.

Give an account of all that happens and test any gas which is evolved with the view of identifying it.

(*e*) Try the action of the strong acid on copper.

(*f*) What is the action of the strong acid on a piece of cloth ?

(*g*) Pour a few drops of acid into a solution of ferrous sulphate and notice the dark coloration which is produced.

All nitrates contain the group of atoms or **radical** (NO_3).

All substances which contain this radical are called "nitrates" and give the following tests.

EXPT. 101.—(1) **Black ring test for a nitrate.**—Take a nitrate and dissolve it in water. Pour into it a little freshly-prepared ferrous sulphate solution. Hold the tube slantwise and slowly pour strong sulphuric acid down the inside of the tube. The sulphuric acid is heavy and flows to the bottom of the tube and forms a separate layer there. At the junction of the two layers a dark brown ring forms.

This reaction is NOT given with dilute sulphuric acid.

(2) Mix some copper turnings with a nitrate and add strong sulphuric acid to the mixture.

If dense brown fumes are evolved a nitrate is present. Free nitric acid is formed by the action of strong sulphuric acid on the nitrate. The nitric acid attacks the copper and gives nitric oxide (NO) which in turn gives brown nitrogen peroxide (NO_2) by combination with the oxygen of the air. (See Demonstration 25.)

$3Cu$	$+$	$8HNO_3$	$=$	$3Cu(NO_3)_2$	$+$	$4H_2O$	$+$	$2NO$
Copper	with	Nitric acid	gives	Copper nitrate	and	water	and	Nitric oxide

$2NO$	$+$	O_2	$=$	$2NO_2$
Nitric oxide	with	Oxygen	gives	Nitrogen peroxide

EXPT. 102.—**Preparation of a nitrite. Test for a nitrite.**—Take a little sodium nitrate and heat it in a small iron vessel with some lead turnings. The mass goes yellow because the lead is oxidised to lead oxide (litharge, PbO) and the sodium nitrate ($NaNO_3$) is reduced to sodium nitrite ($NaNO_2$).

$NaNO_3$	$+$	Pb	$=$	$NaNO_2$	$+$	PbO
Sodium nitrate	with	Lead	gives	Sodium nitrite	and	Lead oxide

Let the fused mass cool and then extract with water. Filter the solution and to it add ferrous sulphate solution and then dilute sulphuric acid. A dark-coloured solution is obtained. The dark colour is due to the same cause as the formation of the black ring in the test given above for a nitrate. In this case the colour was developed with *dilute* sulphuric acid and is due to the presence of a nitrite.

Therefore, suppose ferrous sulphate is added to a given solution, and then dilute sulphuric acid, and a brown colour is developed in the solution, it shows that *a nitrite is present.* If no colour is given with dilute sulphuric acid, but a black ring is formed with strong sulphuric acid, *a nitrate is present.*

EXPT. 103.—**To test for a nitrate and a nitrite in the same solution.**—(1) Warm the given solution with dilute sulphuric acid. Brown fumes are evolved. *A nitrite is suspected.*

(2) To a fresh portion of the solution add ferrous sulphate solution and dilute sulphuric acid. A brown coloration confirms *the presence of a nitrite.*

Take some of the solution and boil it with dilute sulphuric acid till a test sample from it gives no coloration with ferrous sulphate.

Cool the solution which you have been boiling with dilute sulphuric acid.

To it add ferrous sulphate solution and then carefully run strong sulphuric acid down the inside of the tube.

A black ring indicates the presence of a *nitrate.*

Expt. 104.—**Effect of heat on metallic nitrates.**—Heat the given nitrate and tabulate your results. In each case write an account of what happens. Describe the gases which are given off and what the residue is like.

Experiment	Observation.	Inference.
I heated sodium nitrate in a test-tube		
I heated lead nitrate in a test-tube ..		
I heated copper nitrate in a test-tube		
I heated barium nitrate in a test-tube		

Expt. 105.—**Modes of action of nitric acid.**

Nitric acid is an extremely active body and is a powerful oxidising agent.

The following experiments illustrate six different ways in which nitric acid may behave:

(1) **It may have no action at all.**—Test the action of cold and hot nitric acid on the gold leaf supplied to you.

(2) **Passivating action.**—Pour some strong nitric acid on iron

filings. A slight action starts and then stops. The iron will not dissolve it. The iron has assumed the "passive" state. If some water is poured into the tube the action proceeds with violence. One of the conditions necessary for "passivating" by this method is that the nitric acid should be concentrated.

(3) **Formation of an oxide of a metal.**—Take a small piece of tin in a crucible or capsule. Add a few drops of strong nitric acid. A vigorous action takes place. A white powder is formed at the end of the reaction. It is tin oxide (SnO_2).

(4) **Formation of an acid or an acid oxide.**—Boil a small quantity of sulphur with strong nitric acid for a short time. Dilute the solution. Filter. To the filtrate add a solution of barium chloride. A white precipitate is produced in the presence of, and is therefore insoluble in, nitric acid.

This is the test for a sulphate:

$BaCl_2$	+	H_2SO_4	=	$BaSO_4$	+	$2HCl$
Barium chloride	with	Sulphuric acid (or any soluble sulphate)	gives	Barium sulphate	and	Hydro-chloric acid

The nitric acid has oxidised the sulphur to sulphuric acid.

Perform a test to show that barium chloride gives no action with dilute nitric acid.

(5) **Destructive oxidation.**—This takes place with the evolution of brown fumes. (*a*) Treat a piece of cloth with nitric acid and see how the fibre has become quite rotten.

(*b*) Warm a little sugar with strong nitric acid. Brown fumes are evolved and sugar is oxidised to simpler substances.

(6) **Nitration: i.e., introduction of "nitro" (NO_2) group into organic substances.**—Add a few drops of fuming nitric acid to a little benzene in a tube. Pour the mixture into water. Notice the new and pleasant smell of "almond oil." Contrast the smell with the odour of benzene.

The reaction is represented by the equation:

C_6H_6	+	HNO_3	=	$C_6H_5NO_2$	+	H_2O
Benzene	with	strong Nitric acid	gives	Nitro-benzene	and	Water

DEMONSTRATION 25

NITRIC OXIDE AND NITROGEN DIOXIDE

EXPT. 106.—**Nitric oxide.**—In a fume closet fit up a small flask with a thistle funnel and a delivery tube, and arrange to collect the gas over water. The flask is supported on a retort stand. Heating is unnecessary. Put some copper turnings in the flask and fit in the cork, taking great care that it is air-tight. Mix strong nitric acid with an equal volume of water and pour it into the flask through the thistle funnel and observe what happens. The flask is first filled with brown fumes, but as the generation of the gas proceeds the colour gets paler and paler until eventually the flask is quite clear.

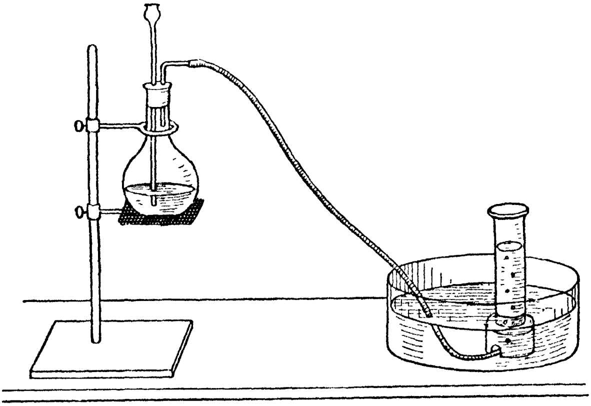


FIG. 60.

Now place the cylinder filled with water over the delivery tube. A *colourless* gas collects in the cylinder. It is nitric oxide—NO.

$3Cu$	$+$	$8HNO_3$	$=$	$3Cu(NO_3)_2$	$+$	$4H_2O$	$+$	$2NO$
Copper	treated with	strong Nitric acid	gives	Copper nitrate	and	Water	and	Nitric oxide

Collect several cylinders of the gas.

EXPT. 107.—**Examine the properties of nitric oxide.**—You cannot smell or taste the gas, because as soon as it comes into contact with air it combines with the oxygen of the air to form a new gas nitrogen dioxide (NO_2).

$2NO$	$+$	O_2	$=$	$2NO_2$
Nitric oxide colourless	with	Oxygen colourless	forms	Nitrogen dioxide (brown gas)

Test whether the gas will burn or support the combustion of a taper. Try to burn several bodies in it by heating them in a deflagrating spoon and thrusting the spoon quickly into a cylinder of the gas. It will be found to support combustion feebly.

It is insoluble in water.

Pass some of the gas into a solution of ferrous sulphate. The solution turns dark brown, almost black. It is to this black solution of nitric oxide in ferrous sulphate that the "black ring" test for a nitrate and the brown coloration test for a nitrite are due.

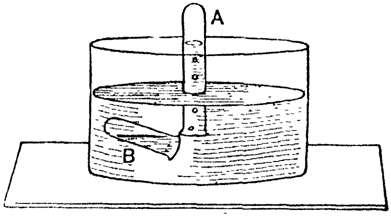


FIG. 61.

A is a test-tube partly filled with air. *B* is a tube partly filled with nitric oxide. Allow a bubble of nitric oxide to enter the tube *A*. Notice what happens. Put the thumb firmly on the mouth of *A* and shake up the tube. (See Fig. 63, page 117.) Replace the mouth of *A* under the water. The brown coloured gas (NO_2) has disappeared. It is soluble in water.

$$2NO + O_2 = 2NO_2.$$

Nitrogen dioxide is formed by the action of heat on certain "heavy nitrates."

EXPT. 108.—**Preparation of nitrogen dioxide.**—Heat some crystals of lead nitrate in a test-tube. Describe all you see and hear, etc. Decrepitation takes place and brown fumes of nitrogen dioxide mixed with oxygen are given off. Smell the gas very cautiously.

$$\underset{\text{Lead nitrate}}{2Pb(NO_3)_2} \underset{\text{on heating gives}}{=} \underset{\text{Lead oxide (litharge)}}{2PbO} \underset{\text{and}}{+} \underset{\text{Nitrogen dioxide}}{4NO_2} \underset{\text{and}}{+} \underset{\text{Oxygen}}{O_2}$$

Collect a few jars of the gas by the downward displacement of air.

EXPT. 109.—**Examine the properties of nitrogen dioxide.**

(1) Test the gas to see if it will burn or support combustion.

(2) Shake up one of the cylinders of gas with litmus solution. What do you observe?

(3) Is the gas soluble in water?

With water, nitrogen dioxide forms a mixture of nitrous and nitric acids.

$$\underset{\text{Nitrogen dioxide}}{2NO_2} \underset{\text{and}}{+} \underset{\text{Water}}{H_2O} \underset{\text{give}}{=} \underset{\text{Nitric acid}}{HNO_3} \underset{\text{and}}{+} \underset{\text{Nitrous acid}}{HNO_2}$$

With caustic soda the sodium salts of nitrous and nitric acids are formed.

$$\underset{\text{Nitrogen dioxide}}{2NO_2} \underset{\text{and}}{+} \underset{\text{Caustic soda}}{2NaOH} \underset{\text{give}}{=} \underset{\text{Water}}{H_2O} \underset{\text{and}}{+} \underset{\text{Sodium nitrite}}{NaNO_2} \underset{\text{and}}{+} \underset{\text{Sodium nitrate}}{NaNO_3}$$

Test the solution obtained by passing nitrogen dioxide into caustic soda ($NaOH$) for the presence of a nitrate and a nitrite (*vide* Expt. 103, page 105).

EXPT. 110.—**Dissociation of nitrogen dioxide.**—Collect a dry test-tube full of nitrogen dioxide by the displacement of air. Cork the tube loosely (*i.e.*, do not push it in so that the tube is shut air-tight). Heat the tube in the Bunsen flame. The colour of the gas deepens until the tube becomes quite opaque. The tube before heating contained some molecules which are made up of two molecules of NO_2 and therefore have the formula N_2O_4. When heated these molecules dissociate into simpler but darker coloured molecules of NO_2.

$$N_2O_4 \rightleftarrows NO_2 + NO_2.$$

The combination of two or more similar molecules to form a more complex molecule is called polymerisation. N_2O_4 is a polymer of NO_2.

When NO_2 is cooled to a temperature of -9° C. it is converted into a colourless liquid (see below).

Nitrogen dioxide is also called nitrogen peroxide.

The only two brown gases you will meet in your course are nitrogen dioxide and bromine.

Nitrogen dioxide can be distinguished from bromine by (1) its smell, (2) it gives a brown-coloured solution when passed into ferrous sulphate solution. Bromine does not do this.

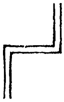
Confirm this by experiment.

DEMONSTRATION

Liquefaction of nitrogen dioxide.

DEMONSTRATION 26

AMMONIA

Expt. 111.—**Preparation of ammonia.**—Fit up a flask with a tube bent twice at right angles  Fit the flask in a stand and set it in a sand-bath.

Arrange a piece of cardboard with a hole through it on the ring of a retort stand and fixed at such a height that the free end of the tube from the flask can pass through it. The apparatus should be arranged as shown in Fig. 62. It is better to conduct the experiment in a fume closet or under a hood.

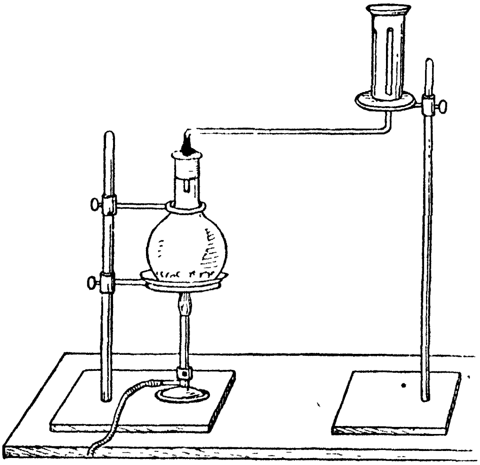


Fig. 62.

Pound up each of the two substances given to you separately in a mortar. One is an ammonium salt and the other is lime, *i.e.*, calcium oxide (CaO). Pour a little water into the flask. Now mix the substances on a piece of paper. Do you notice that any odour is given out? Put the mixture in the flask and fit up the apparatus. Heat the flask and collect the gas in a *dry* cylinder by upward displacement of air as illustrated above. You can ascertain when the cylinder is full of gas by putting a piece of moist pink litmus paper near where the delivery tube passes through the cardboard. When the litmus turns blue the cylinder is full. Remove the cylinder and close it with a cover-glass. Place another dry cylinder over the tube. The lime acts on ammonium salt thus:—

$2NH_4Cl$	$+$	$Ca(OH)_2$	$=$	$CaCl_2$	$+$	$2NH_3$	$+$	$2H_2O$
Ammonium chloride	acted on by	Lime	gives	Calcium chloride	and	Ammonia	and	Water

EXPT. 112.—**Observe the properties of the gas.**

Tabulate your results.

(1) It is colourless.

(2) It has a peculiar and pungent smell.

(3) Ascertain whether it is a supporter of combustion and if it burns.

(4) Invert a cylinder in water. Is the gas soluble?

(5) What is its reaction to litmus solution?

(6) Shake up a few drops of hydrochloric acid in a clean cylinder. Invert it over a cylinder of ammonia. What happens? Why?

(7) Put a piece of moist turmeric paper in the gas. What happens?

You are given a solution of ammonia in water.

EXPT. 113.—**Action of ammonia on copper sulphate solution.**—Ammonia solution gives a bright blue coloration with a solution of copper sulphate.

EXPT. 114.—**Ammonium hydroxide exists in solution.**—Test in the solution of ammonia for the "hydroxyl" group (*i.e.*, ion), (1) with litmus, (2) with phenolphthalein, (3) with ferric chloride solution. (See Demonstration 11, page 57.)

When ammonia dissolves in water the solution contains a substance called ammonium hydrate or hydroxide (NH_4OH).

$$NH_3+H_2O=NH_4OH.$$

The group (NH_4) "ammonium" possesses distinct properties of its own. It is capable of being transferred from one compound to another and is called a "compound radical." It behaves like a metal and is therefore called a "basic" radical.

There are many such radicals and several have already been mentioned:

e.g.	$(NO_3)'$	a monobasic acid radical	(nitric acid).
	$(CH_3COO)'$	,, ,,	(acetic acid).
	$(CO_3)'$	a dibasic acid radical	(carbonic acid).
	$(SO_4)''$	,, ,,	(sulphuric acid).
	$(HPO_3)''$	,, ,,	(phosphorous acid).
	$(PO_4)'''$	a tribasic acid radical	(phosphoric acid).

EXPT. 115.—**Tests for ammonia.**—*The test for ammonia* depends upon the facts that it is the only GAS in your course which
(1) has the peculiar smell of ammonia,
(2) turns red litmus blue,
(3) turns turmeric paper brown.

EXPT. 116.—**Testing "unknown" substances for ammonia.**—Test the given salts by boiling them with sodium hydroxide. All ammonium salts give off ammonia gas when warmed with sodium hydrate.

EXPT. 117.—**Ammonia is produced when feathers are subjected to dry distillation.**—Heat some feathers in a test-tube and show that ammonia is among the volatile products of the dry distillation.

EXPT. 118.—**Action of heat on ammonium salts.**—Heat the given ammonium salts and write, in tabular form, notes on what you observe and the conclusions you come to in each case.

NOTE ON THE TEST FOR HYDROXIDES

Solutions of some normal salts, *e.g.*, Na_2CO_3, give the test for the "hydroxyl" group (ion). The group does not exist in the salt itself, but is due to the partial decomposition (hydrolysis) of the salt when it is dissolved in water and therefore does exist in the solution. *If no acid radical can be detected by the systematic examination which will be given in the sequel and the solution gives the tests for the hydroxyl group, then the presence of a soluble hydroxide is indicated.* The original substance may have been an oxide or an hydroxide. If, on heating dry, the substance is not a salt, and it gives off water vapour, it was an hydroxide.

DEMONSTRATIONS

(1) You will be shown that when ammonia is heated with air it will burn.

(2) The solubility of ammonia by the "fountain experiment."

(3) The *adsorption* of ammonia by charcoal (*vide* Demonstration 5, Expt. 28, page 29).

Draw sketches of the apparatus used and make notes on the way in which the experiments are conducted.

DEMONSTRATION 27

Nitrous Oxide and Nitrogen

Nitrous Oxide

When ammonia gas is passed into nitric acid a salt of nitric acid called ammonium nitrate is formed.

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Nitric acid}}{HNO_3} = \underset{\text{Ammonium nitrate}}{NH_4{\cdot}NO_3}$$

When this substance is heated it decomposes, giving a new oxide of nitrogen called nitrous oxide (N_2O).

$$\underset{\substack{\text{Ammonium}\\ \text{nitrate}}}{NH_4{\cdot}NO_3} \underset{\substack{\text{decomposes}\\ \text{into}}}{=} \underset{\text{Steam}}{2H_2O} \underset{\text{and}}{+} \underset{\substack{\text{Nitrous}\\ \text{oxide}}}{N_2O}$$

EXPT. 119.—**Preparation of nitrous oxide.**—Fit a boiling tube with a wide-bore delivery tube. Let this delivery tube lead to an evaporating basin containing *hot* water in which a tube containing hot water is inverted. The gas will be collected in the test-tube.

Put some crystals of ammonium nitrate in the boiling tube and fit the cork in tightly. Now, having placed the end of the delivery tube under the test-tube in the evaporating basin carefully, heat the ammonium nitrate with a Bunsen flame. Notice what happens. As soon as the gas begins to come off, stop heating until the action has subsided. At first the gas will be contaminated with air, but after a short time the collecting tubes will contain practically pure nitrous oxide. Collect several tubes of the gas.

EXPT. 120.—**Examine the properties of nitrous oxide.**

(1) Describe the gas, giving its colour, smell, etc.

(2) Test the gas to see if it is soluble in cold water.

(3) Shake some of the gas up with ferrous sulphate solution. What happens?

(4) Does the gas support combustion? Does it burn?

(5) What is its action when shaken up with litmus solution?

After carefully examining the properties of nitrous oxide we shall find that it possesses the following properties in common with oxygen.

It is a colourless gas, neutral to litmus, and is a supporter of combustion.

No other gas possesses all these properties. It is true that nitrous oxide has a sweet smell, but it is difficult to distinguish it from oxygen by that test.

EXPT. 121.—**To distinguish oxygen from nitrous oxide.**—On the demonstration table you will find inverted in water three sets of tubes.

Those labelled *A* are partially filled with oxygen.
" " *B* " " " " nitrous oxide.
" " *C* " " " " nitric oxide.

Lift one of each carefully out by placing your thumb tightly at the mouth (see figure) and transfer them to your own pneumatic trough on your bench. The water in the tube acts as an air-tight seal, held in place by your thumb.

(1) Now let a little of nitric oxide from tube *C* bubble into tube *A* (see Fig. 61, page 109). The gas in *A* will turn brown. (2) Let a little of nitric oxide from *C* bubble into the tube *B* containing nitrous oxide. There is no coloration developed in the tube.

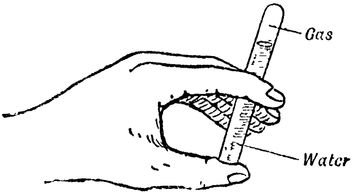


FIG. 63.

The distinction between nitrous oxide and oxygen is that *oxygen gives a brown coloration with nitric oxide, nitrous oxide gives no coloration with nitric oxide.*

Nitrogen

Ammonia combines with nitrous acid to form ammonium nitrite.

$$\underset{\text{Ammonia}}{NH_3} \quad \underset{\text{and}}{+} \quad \underset{\text{Nitrous acid}}{HNO_2} \quad \underset{\text{form}}{=} \quad \underset{\text{Ammonium nitrite}}{NH_4 \cdot NO_2}$$

When ammonium nitrite is heated it decomposes irreversibly, giving nitrogen and steam.

$$\underset{\substack{\text{Ammonium}\\\text{nitrite}}}{NH_4 \cdot NO_2} \quad \underset{\substack{\text{decomposes}\\\text{into}}}{=} \quad \underset{\text{Nitrogen}}{N_2} \quad \underset{\text{and}}{+} \quad \underset{\text{Steam}}{2H_2O}$$

The direct heating of ammonium nitrite is apt to result in explosion. For this reason it is better to heat a solution of sodium nitrite with an excess of ammonium chloride. If the ammonium chloride is not in excess explosions are likely to occur.

Expt. 122.—**Preparation of nitrogen.**—The solution *E* is sodium nitrite and the solution *F* is ammonium chloride. The strengths of the two solutions are so arranged that if you take equal volumes of *E* and *F*, the ammonium chloride will be in excess.

Mix equal volumes of the two solutions in a flask provided with a delivery tube which leads under a cylinder filled with water and inverted in a pneumatic trough filled with water. Fit the flask in a retort stand and heat it on a sand-bath. Nitrogen gas will be given off and will collect in the cylinder by displacement of water.

The reaction which takes place may be represented by two equations.

$$(1) \quad \underset{\substack{\text{Ammonium}\\\text{chloride}}}{NH_4Cl} \quad \underset{\text{with}}{+} \quad \underset{\substack{\text{Sodium}\\\text{nitrite}}}{NaNO_2} \quad \underset{\text{give}}{=} \quad \underset{\substack{\text{Ammonium}\\\text{nitrite}}}{NH_4 \cdot NO_2} \quad \underset{\text{and}}{+} \quad \underset{\substack{\text{Sodium}\\\text{chloride}}}{NaCl}$$

$$(2) \qquad NH_4 \cdot NO_2 = N_2 + 2H_2O$$

or, writing the two equations in one,

$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2.$$

Expt. 123.—**Observe the properties of the gas.**

(1) It is a colourless, tasteless, odourless gas.

(2) It is a non-supporter of combustion. (Try several substances, *e.g.*, S, C, Mg, etc.)

(3) It is neutral to litmus.

(4) It gives no reaction with ferrous sulphate solution.

(5) It does not bleach. It gives no coloration with nitric oxide.

(6) It has no action on lime-water (distinction from carbon dioxide).

EXPT. 124.—**Identification of gases.**—Heat the given substances *G*, *H*, *J*, *K* in a test-tube, and in each case detect what gas is given off (if any).

(Any of the gases dealt with up to the present stage of study may be expected. They comprise oxygen, hydrogen, hydrochloric acid, chlorine, carbon dioxide, carbon monoxide, nitric oxide, nitrogen dioxide, nitrous oxide and nitrogen.)

Tabulate your results.

DEMONSTRATIONS

(1) When air is passed over red-hot copper the copper combines with the oxygen of the air and "atmospheric" nitrogen passes over. "Atmospheric" nitrogen is not pure nitrogen. The copper oxide is heated in a hard glass tube in a furnace.

$$\underset{\text{Copper}}{2Cu} \quad \underset{\text{combines with}}{+} \quad \underset{\text{Oxygen}}{O_2} \quad \underset{\text{giving}}{=} \quad \underset{\text{Copper oxide}}{2CuO}$$

(2) Phosphorus will be burnt in a bell jar inverted in a trough of water.

The volume of air should be marked before the phosphorus is lighted. After the experiment it will be found that the residual nitrogen occupies about four-fifths of the space originally occupied by air.

Draw diagrams of the apparatus and describe the experiment briefly.

Notes to Demonstrators

For *E* and *F* dissolve equal weights of sodium nitrite and ammonium chloride in equal volumes of tap water. The solutions should be as concentrated as possible.

For *G*, *H*, *J*, *K*, etc., give such substances as potassium chlorate, ammonium carbonate, sodium oxalate, sodium carbonate, ammonium nitrate, lead nitrate, red lead, etc.

DEMONSTRATION 28

SULPHUR

PHOSPHORUS AND PHOSPHORIC ACID

EXPT. 125.—**Ordinary roll sulphur.**—(*a*) Examine the given specimen. Give an account of its properties. Notice how brittle it is.

(*b*) Put a little in a test-tube and heat the tube very gently by holding it at some little distance from the flame at first. It melts to a pale yellow, mobile liquid which is quite clear. On further heating it darkens in colour and at the same time becomes viscous (*i.e.*, thick and difficult to pour). Eventually it becomes almost black. The substance becomes so thick that the tube can be inverted. Continue heating and it will be found that its density again diminishes and it can be poured into cold water. This converts the sulphur into an allotropic modification called **plastic sulphur.**

EXPT. 126.—**Plastic sulphur.**—An " elastic " substance is one which, when deformed from its ordinary shape by the application of an external force, will resume its former shape when relieved of the force which was applied to it. " Plastic " substances can be deformed by the application of a force, but do not reassume their former shape when relieved of the force.

If plastic sulphur is allowed to stand, the sulphur becomes hard and loses its plastic property.

EXPT. 127.—**Flowers of sulphur** are produced by heating sulphur till it boils and then condensing the vapour on a cold surface.

EXPT. 128.—**Rhombic sulphur.**—Dissolve some roll sulphur in a little carbon disulphide in a test-tube. Filter the solution into a small basin and set it on one side. The solvent carbon disulphide evaporates and leaves pale yellow crystals of "rhombic sulphur" on the walls of the basin.

Select a good crystal and make a sketch of it. Use a lens if necessary.

EXPT. 129.—**Prismatic sulphur** will be prepared before the class by the demonstrator.

Sulphur is added in small quantities to a small vessel which is gently heated. The sulphur is melted but *should not be allowed to darken.* Careful heating is essential. The temperature of the molten sulphur should not rise above 120° C. When sufficient sulphur has been melted and the liquid is limpid and of a pale yellow or amber colour, remove the vessel from the burner. Allow the liquid to cool and a crust will be seen to form over the surface of it.

Break two holes through this crust and through one pour off what sulphur still remains in the molten condition. Cut away what remains of the crust. Fine needles of "prismatic sulphur" will be seen standing vertically on the walls of the beaker. These needles change into the rhombic form on standing for some time.

EXPT. 130.—**Milk of sulphur** is formed when a solution of polysulphides is treated with dilute hydrochloric acid. (Add the acid to the polysulphides.)

A second method.—Mix a solution of sulphuretted hydrogen with solution of sulphur dioxide.

$$2H_2S + SO_2 = 2H_2O + 3S.$$

From the above experiments you learn that sulphur can exist in several forms. When an *element* can exist in more than one distinct form, each form having different physical properties, the element is said to exhibit "allotropy." The various different forms are called "allotropic" modifications of the element.

This property has already been observed in the case of carbon (Demonstration 15, page 73).

When sulphur combines with another element the compound formed is called a **sulphide.** Sulphides may often be formed "synthetically," *i.e.*, built up from their elements.

Expt. 131.—Heat a mixture of sulphur (4 parts) and iron (7 parts). When the action starts remove the tube from the burner.

Describe carefully all that happens.

The substance formed is iron sulphide.

Fe	$+$	S	$=$	FeS
Iron	with	Sulphur	gives	Ferrous sulphide

Expt. 132.—**Action of nitric acid on sulphur.**—Show that when sulphur is heated with nitric acid sulphuric acid is formed.

Phosphorus

Phosphorus also exhibits the property of allotropy.

Expt. 133.—**Compare the properties of the two forms of phosphorus.**

Write the report in tabular form.

(1) Yellow phosphorus.

(2) Red or amorphous phosphorus.

Properties.	Yellow phosphorus	Red phosphorus.
Description		
Colour		
Smell		
Solubility in water .. .. ,, in carbon disulphide		
Inflammability		
Phosphorescent (take the specimen into the dark room)		

Expt. 134.—**Nitric acid oxidises phosphorus to phosphoric acid.**—Boil some red phosphorus with nitric acid. Let any unattacked phosphorus settle and then pour off the liquid into another tube. Boil some ammonium molybdate solution with nitric acid.

Mix these two liquids together and boil again.

A yellow precipitate indicates the presence of phosphoric acid.

If the yellow precipitate does not form at once, stand the tube on one side. The precipitate should appear in a few minutes.

This reaction is given by all phosphates.

DEMONSTRATION 29

SULPHURETTED HYDROGEN, HYDROGEN SULPHIDE, H_2S

PREPARATION OF SULPHURETTED HYDROGEN

EXPT. 135.—**Prepare this gas in a fume closet.**—Fit up an apparatus like that used in (Fig. 50) the preparation of carbon dioxide gas (Demonstration 16, page 75). The gas must be collected by displacement of air as it is soluble in water. It may be collected over hot water, but the first method is more satisfactory. Put some water in the bottom of the Woulfe's bottle and then some small pieces of ferrous sulphide. Fit in the cork and pour hydrochloric acid or dilute sulphuric acid into the bottle through the thistle funnel. The tube of the thistle funnel must dip below the liquid in the bottle.

Write an equation representing the action.

Collect several cylinders of the gas.

EXPT. 136.—**Examine the properties of the gas.**

(1) Observe (i) its colour.
(ii) its smell.
(iii) its action on litmus.
(iv) its solubility.

(2) Is the gas a supporter of combustion or does it burn ?

(3) Does it turn lime-water milky ?

(4) Dip a piece of paper in lead acetate solution and then put it in the gas. The paper is turned black owing to formation of lead sulphide (PbS).

This constitutes a test for sulphuretted hydrogen gas.

$$\underset{\text{Lead acetate}}{(CH_3\cdot COO)_2Pb} \quad \underset{\text{with}}{+} \quad \underset{\substack{\text{Sulphur-}\\\text{etted}\\\text{hydrogen}}}{H_2S} \quad \underset{\text{gives}}{=} \quad \underset{\text{Acetic acid}}{2CH_3\cdot COOH} \quad \underset{\text{and}}{+} \quad \underset{\substack{\text{Lead}\\\text{acetate}}}{PbS}$$

(5) The presence of the gas in solution may be detected by shaking the solution up with a suspension of cadmium carbonate in water. If the suspension turns yellow the presence of sulphuretted hydrogen in solution is indicated. It has converted the white carbonate into cadmium sulphide, which is yellow.

$CdCO_3$	$+$	H_2S	$=$	CdS	$+$	H_2O	$+$	CO_2
Cadmium carbonate (white)	with	Sulphuretted hydrogen	gives	Cadmium sulphide (yellow)	and	Water	and	Carbon dioxide

Lead carbonate may also be used. In this case the white suspension is turned black (PbS) by the action of the sulphuretted hydrogen in the solution.

The presence of carbon dioxide does not interfere with this test.

Expt. 137.—**Test for all sulphides.**—(1) Heat any sulphide strongly with sodium carbonate under the blowpipe. Remove the fused mass and put it on a silver coin. Moisten the mass with water. If the coin turns black there was sulphide present. The coin turns black (tarnishes) because the surface of the silver is converted into sulphide.

(2) If a sulphate is heated with sodium carbonate and carbon, the carbon reduces the sulphate to sulphide and the above test for a sulphide is given.

A **kipp** is an apparatus by the use of which a continuous stream of sulphuretted hydrogen may be obtained. (See Fig. 64.)

Bulb No. 1 is in direct and continuous connection with the tube which passes to the bottom of the apparatus. The joint at *A* is air-tight.

In bulb No. 2 ferrous sulphide in the form of short sticks is placed. The ferrous sulphide is prevented from slipping into the lowest bulb by the perforated collar at *B*. The bulb No. 2 is fitted with a glass tap. Acid is poured in through the thistle funnel and falls into the bulb 3. Open the tap and the acid rises to the bulb No. 2. Here it finds the ferrous sulphide and attacks it, forming sulphuretted hydrogen which passes through the tap. Turn off the tap. The gas continues to be generated so long as the acid is in contact with the sulphide. As the tap is turned off the pressure inside No. 2

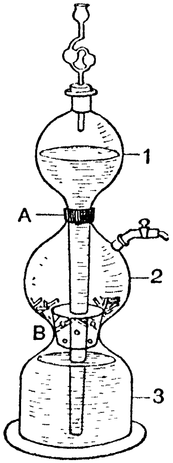


Fig. 64.

increases and forces the acid out of No. 2, and up into No. 1. The action now stops. When gas is required the tap is turned on and a plentiful supply is obtained.

By using marble and hydrochloric acid or zinc and hydrochloric acid a continuous stream of carbon dioxide or hydrogen respectively may be obtained in a similar apparatus.

For the following experiments use the supply of sulphuretted hydrogen from a "kipp."

EXPT. 138.—**Action of sulphuretted hydrogen on the given solutions.**—Pass the gas through the following solutions (*A*—*G*) and try to write equations representing the changes taking place in each of the reactions.

In each case describe in your note-book all that happens.

Write your results in tabular form.

(*A*) Zinc sulphate ($ZnSO_4$) solution (acid).

" " " " (alkali).

(*B*) Copper sulphate ($CuSO_4$) solution (acid).

(*C*) Arsenious acid (H_3AsO_3) in presence of HCl.

(*D*) Solution of iodine in water.

(*E*) Ferric chloride ($FeCl_3$) solution (acid).

(*F*) Potassium permanganate ($KMnO_4$) with dilute sulphuric acid.

(*G*) Sulphurous acid (H_2SO_3). The correct equations will be found at the end of the demonstration.

DEMONSTRATION

You will be shown another apparatus (Fig. 65) for obtaining a continuous supply of sulphuretted hydrogen as required. *A* and *B* are two aspirators connected by a rubber tube on which is slipped a pinch-cock. This may be used to close the connecting tube when necessary.

The mouth of *A* is open, but it may have a guard tube fixed in it. Acid (dilute HCl or H_2SO_4) is in *A* and sulphide in *B*. The clip *C* is open. To generate the gas raise *A* on the block as shown. Open the tap *D*. Acid runs into *B* and generates the gas. The vessel into which it is desired to pass the gas is connected to *D* by a rubber tube. To stop the generation of the gas: Turn off the tap at *D* and put *B* on the block and *A* on the table. The acid runs from *B* to *A* and the action ceases.

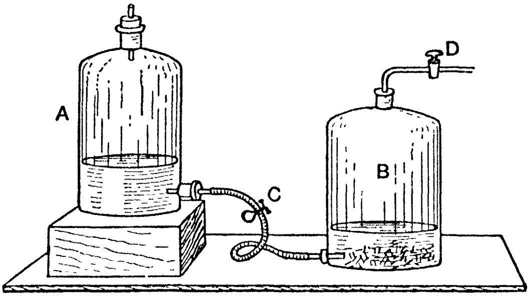


FIG. 65.

Equations

Expt. 136 (2). Partial combustion.

$2H_2S$	+	O_2	=	$2S$	+	$2H_2O$
Sulphuretted hydrogen	with	Oxygen	gives	Sulphur	and	Water

Complete combustion.

$2H_2S$	+	$3O_2$	=	$2SO_2$	+	$2H_2O$
				Sulphur dioxide		

Expt. 137. Test for a sulphide.

Na_2CO_3	+	PbS	=	Na_2S	+	PbO	+	CO_2
Sodium carbonate	heated with	Lead sulphide	gives	Sodium sulphide	and	Lead oxide	and	Carbon dioxide

Expt. 138. Reactions with sulphuretted hydrogen on salt and other solutions.

(*A*) Zinc sulphate in acid solution—no action.

In alkaline solution

$ZnSO_4$	+	H_2S	=	ZnS	+	H_2SO_4
Zinc sulphate		Sulphuretted hydrogen		Zinc sulphide (white precipitate)		This acid is neutralised by the alkali present

(*B*)	$CuSO_4$	+	H_2S	=	CuS	+	H_2SO_4
	Copper sulphate				Copper sulphide (black precipitate)		

(*C*) $$\underset{\substack{\text{Arsenious}\\ \text{acid}}}{2H_3AsO_3} + HCl + 3H_2S = \underset{\substack{\text{Ammonium}\\ \text{sulphide}\\ \text{(yellow}\\ \text{precipitate)}}}{As_2S_3} + HCl + 6H_2O$$

(*D*) $$\underset{\substack{\text{Iodine}\\ \text{(brown solution)}}}{I_2} + H_2S = \underset{\substack{\text{Hydriodic acid}\\ \text{(colourless)}}}{2HI} + \underset{\substack{\text{Sulphur}\\ \text{(white precipitate)}}}{S}$$

(*E*) $$\underset{\substack{\text{Ferric chloride}\\ \text{(yellow}\\ \text{solution)}}}{2FeCl_3} + H_2S = \underset{\substack{\text{Ferrous chloride}\\ \text{(pale green}\\ \text{solution)}}}{2FeCl_2} + 2HCl + \underset{\substack{\text{Sulphur}\\ \text{(white}\\ \text{precipitate)}}}{S}$$

(*F*) $$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

Purple solution turns colourless and sulphur is precipitated.

(*G*) $$\underset{\text{Sulphurous acid}}{H_2SO_3} + 2H_3S = \underset{\text{Sulphur}}{3S} + \underset{\text{Water}}{3H_2O}$$

DEMONSTRATION 30

SULPHUR DIOXIDE

SULPHITES AND THIOSULPHATES

The equations representing the reactions which take place will be found at the end of the demonstration.

EXPT. 139.—**Preparation of sulphur dioxide.**—Fit up an apparatus like that used for the preparation of hydrochloric acid gas (Fig. 47, page 61). Place a piece of gauze under the flask. See that the delivery tube dips to the bottom of the cylinders. Take care that the cylinders used for the collection of the gas are dry. Into the flask put some copper turnings and fit the cork in tightly. *The apparatus should be set up in a fume closet, as the fumes of the gas are very irritating and objectionable.* Now pour sufficient sulphuric acid through the thistle funnel to cover the copper turnings and the end of the thistle funnel tube. Heat with a Bunsen burner until the acid just boils and the gas is coming off. Then lower the gas until the heat is just sufficient to keep the stream of gas coming steadily.

Write the equation for what happens.

Collect several cylinders of the gas. You can tell when the cylinder is full either by the fact that a match put near the cylinder of the gas is extinguished or by the action of the gas on moist blue litmus paper. The colour is turned to pink when the cylinder is full.

EXPT. 140.—**Observe the properties of the gas. Tabulate your results.**

(1) The gas is colourless.

(2) It has a powerful and irritating odour. The smell is usually

described as the smell of "burning sulphur." Take care to smell it very cautiously. If you inhale too much of the gas the result is very painful.

If, by accident, you inhale the gas and feel any distress, go into the open air and breathe deeply. Call to the laboratory assistant for boiling water and breathe the steam. It will give you some relief.

(3) See if it is soluble in water by inverting a cylinder full of the gas in a trough of water.

(4) Pass some of the gas into water. Taste a drop of the water afterwards.

(5) Ascertain whether gas supports combustion or burns.

(6) Shake some flowers up with the gas. What happens?

Now moisten some flowers with water and shake them up with the gas. The flowers are bleached after a short time. This bleaching is due to reduction ($SO_2+2H_2O=H_2SO_4+2H_2$), whereas the bleaching action of chlorine is due to oxidation ($2Cl_2+2H_2O=4HCl+O_2$).

The colour bleached by chlorine cannot be restored, but when a colour has been bleached by sulphur dioxide it can often be restored by shaking the bleached flowers with dilute sulphuric acid. The "restored" colour is not always the same shade or colour as it was originally.

Shake your bleached flowers with dilute sulphuric acid and describe all you see.

(7) Shake some litmus solution in a cylinder of the gas. What do you see?

EXPT. 141.—**Reducing action of sulphur dioxide.**—(8) Pass sulphur dioxide gas through the following solutions. Write equations.

A. Potassium dichromate acidified with dilute sulphuric acid.
B. Potassium permanganate acidified with dilute sulphuric acid.
C. Sulphuretted hydrogen (hydrosulphuric acid) in water.

EXPT. 142.—**Test for sulphur dioxide.**—Into the gas put a piece of filter paper moistened with an acid solution of potassium dichromate. If the colour turns from yellow to green or bluish-green,

Sulphur dioxide is present.

Apply this test to the following reactions :

(1) Heat zinc with strong sulphuric acid.
(2) „ carbon „ „ „
(3) „ sulphur „ „ „
(4) Heat " hypo " with dilute sulphuric acid.

Write equations for the reactions which take place.

When sulphur dioxide dissolves in water " sulphurous acid " is formed.

SO_2	$+$	H_2O	$=$	H_2SO_3
Sulphur dioxide	combines with	Water	to form	Sulphurous acid

The formula H_2SO_3 shows that the acid contains two atoms of hydrogen. Both these atoms of hydrogen are replaceable by a metal (or its equivalent). The acid is therefore dibasic acid, and forms two series of salts. (See Demonstration 17, page 79) :

(1) Acid sulphites or bisulphites, *e.g.*, $NaHSO_3$.
(2) Normal sulphites, *e.g.*, Na_2SO_3.

Expt. 143.—**Tests for sulphites.**—Write equations. (1) All sulphites, when treated with dilute hydrochloric acid, give off sulphur dioxide gas. There is no separation of sulphur.

The gas is detected by (1) its smell ; (2) the bichromate test (see above, Expt. 141, *A*).

(2) To a solution of a sulphite add barium chloride solution. A white precipitate of barium sulphite ($BaSO_3$) comes down. This precipitate is soluble in dilute hydrochloric acid with evolution of SO_2.

(3) Add bromine water to a solution of a sulphite. The bromine water is decolorised. Boil off any excess of bromine. To the solution add barium chloride solution. White precipitate. To the precipitate add HCl and warm. The precipitate is insoluble and no SO_2 is evolved. Therefore sulphite is absent. The precipitate is barium sulphate. The sulphite was oxidised to sulphate by bromine water.

Note.—All acids the names of which end in **ous** form salts the names of which end in **ite.**

*Sulphur***ous** acid gives a *sulph***ite.**
*Chlor***ous** acid gives a *chlor***ite.**
*Phosphor***ous** acid gives a *phosph***ite.**

When an acid the name of which ends in **ous** is oxidised it forms an acid the name of which ends in **ic.** The names of salts of acids the names of which end in "ic" have the termination **ate**, *e.g.*, sulphur*ous* acid on oxidation yields "sulphur*ic*" acid, which in turn gives salts called "sulph*ates*."

The nomenclature is quite regular, *e g.*, for a typical case of an acid exhibiting progressive oxidation—that of the chlorine acids.

The "stem" of the words is printed in black and the prefixes and suffixes which are peculiar to the degree of oxidation are printed in italics.

*Hydro***chlor***ic*	acid,	HCl,	gives	**chlor***ides.*
*Hypo***chlor***ous*	acid,	$HClO$,	gives	*hypo***chlor***ites.*
chlor*ous*	acid,	$HClO_2$,	gives	**chlor***ites.*
chlor*ic*	acid,	$HClO_3$,	gives	**chlor***ates.*
*Per***chlor***ic*	acid,	$HClO_4$,	gives	*per***chlor***ates.*

If the oxygen of an acid is partly or completely substituted by sulphur the prefix **thio** is written in front of the name of the acid, *e.g.*, if the oxygen of sulphuric acid, H_2SO_4, is partly replaced by sulphur we get an acid, $H_2S_2O_3$, called "thiosulphuric" acid. Similarly, if the oxygen of arsenious acid, H_3AsO_3, is completely replaced by sulphur the acid H_3AsS_3, or "thioarsenious acid," is produced.

Expt. 144.—**Preparation of a thiosulphate.**—Boil some sodium sulphite solution with flowers of sulphur for a few minutes. Filter the solution. The crystals of the substance formed will have the formula $Na_2S_2O_3,5H_2O$, sodium thiosulphate or "hypo," produced by the addition of sulphur to sodium sulphite.

Na_2SO_3	+	S	=	$Na_2S_2O_3$
Sodium sulphate	and	Sulphur	give	Sodium thiosulphate

Warm some of the filtrate with dilute hydrochloric acid. SO_2 is evolved (test) and *yellow sulphur is deposited.*

The simultaneous evolution of sulphur dioxide and separation of sulphur is a reaction peculiar to *thiosulphates.* For these experiments use the "hypo" or commercial sodium thiosulphate provided.

Expt. 145.—**Tests for a thiosulphate.**

(1) Warm some "hypo" dry in a test-tube. Show that both SO_2 and H_2S are evolved.

(2) Treat a solution of " hypo " in water with dilute hydrochloric (or sulphuric) acid. SO_2 is evolved (test) and a yellow precipitate of sulphur is thrown down (distinction from a sulphite).

(3) Add barium chloride solution to a solution of " hypo." No precipitate is formed (distinction from sulphate and sulphite).

Equations

Expt. 139.—**Preparation of sulphur dioxide.**

$2H_2SO_4$	+	Cu	=	$CuSO_4$	+	$2H_2O$	+	SO_2
Sulphuric acid	and	Copper	give	Copper sulphate	and	Water	and	Sulphur dioxide

Expt. 141.—**Reducing action of sulphur dioxide.**

(*A*)	$K_2Cr_2O_7$	+	H_2SO_4	+	$3H_2O$	+	$3SO_2$	
	Potassium dichromate (yellow)		Sulphuric acid		Water		Sulphur dioxide	
	=	$Cr_2(SO_4)_3$	+	K_2SO_4	+	$4H_2O$		
	react to give	Chromium sulphate (green)		Potassium sulphate		Water		

(*B*)	$2KMnO_4$	+	$5H_2O$	+	$5SO_2$			
	Potassium permanganate		Water		Sulphur dioxide			
=	$2H_2SO_4$	+	K_2SO_4	+	$2MnSO_4$	+	$3H_2O$	
give	Sulphuric acid		Potassium sulphate		Manganese sulphate		Water	

(*C*)	$2H_2S$	+	SO_2	=	$2H_2O$	+	$3S$	
	Sulphuretted hydrogen	and	Sulphur dioxide	give	Water	and	Sulphur	

Expt. 142.—**Action of sulphuric acid on certain substances.**

$$Zn+H_2SO_4=ZnSO_4+2H_2O+SO_2$$
$$C+2H_2SO_4=2H_2O+CO_2+2SO_2$$
$$S+2H_2SO_4=2H_2O+3SO_2$$
$$Na_2S_2O_3+H_2SO_4=Na_2SO_4+H_2O+SO_2+S$$

Expt. 143 (3).—**Oxidation of a sulphite to a sulphate by bromine water.**

Br_2	+	H_2O	+	Na_2SO_3	=	Na_2SO_4	+	$2HBr$
Bromine		Water		Sodium sulphite		Sodium sulphate		Hydrobromic acid

DEMONSTRATION 31

TESTS FOR SULPHUR ACIDS

I use the term "sulphur" acid to mean acids containing sulphur in their constitution, *cf.* chlorine acid.

Write equations representing the actions which take place.

EXPT. 146.—**Tests for hydrosulphuric acid and sulphides.**—Revise the tests for hydrosulphuric acid (sulphuretted hydrogen) given in Expts. 136 and 137, page 125. Use solid or solution *A* (Na_2S).

EXPT. 147.—**Tests for sulphurous acid and sulphites.**—Revise the tests for sulphurous acid given in Expt. 143, page 131. Use solid or solution *B* (Na_2SO_3).

EXPT. 148.—**Tests for thiosulphuric acid and thiosulphates.**—Revise the tests for thiosulphuric acid given in Expt. 145, page 132. Use solid or solution *C* ($Na_2S_2O_3$).

EXPT. 149.—**Tests for sulphuric acid.**—(i) *Vide* Expt. 137 (2), page 125. Use (Na_2SO_4). (ii) To the solution *D* (Na_2SO_4) add barium chloride ($BaCl_2$) solution. A heavy, white precipitate of barium sulphate ($BaSO_4$) is thrown down. It is insoluble in hydrochloric acid. (iii) To the solution *D* add a solution of lead acetate [$(CH_3 \cdot COO)_2\,Pb$]. A white precipitate of lead sulphate is thrown down. The lead sulphate is soluble in ammonium acetate solution.

EXPT. 150.—Test the substances *E*, *F*, *G*, and find out if any sulphur acid is present, and if so which is present of the four acids the tests of which are given above?

METHOD :—

Experiment	Observation.	Inference.
A. Warm the substance with dilute hydrochloric acid.	1 No action.	No *sulphur acid* at all or possibly a sulphate.
	2. SO_2 evolved (test). Solution clear.	A *sulphite* is present.
	3. SO_2 evolved (test). A precipitate of sulphur is thrown down.	A *thiosulphate* is present.
	4. H_2S evolved (test with lead acetate paper).	A *sulphide* is present.

The substance is soluble in water.

Experiment.	Observation.	Inference.
B. Shake the solution with cadmium carbonate. *Or*—	Suspension goes yellow	*Sulphide* present.
Shake solution with lead carbonate	Suspension goes black.	
To the solution add barium chloride solution.	No precipitate.	*Sulphide* or *thiosulphate* may be present. (See above)
	White precipitate (1) Soluble in HCl SO_2 evolved (test). Solution clear.	*Sulphite* present.
	(2) Soluble in HCl. SO_2 evolved (test) (Solution contains sulphur.)	*Thiosulphate* present.
	(3) Insoluble in HCl. (boiling).	*Sulphate* present.
To solution add solution of iodine in potassium iodide.	Solution is decolorised. No precipitate.	*Thiosulphates* and *sulphites* do this.

The substance is insoluble in water.

Boil the substance with strong sodium carbonate solution. Filter. Double decomposition will take place and the sodium salt of the acid will exist in the solution together with excess of sodium carbonate.

Experiment.	Observation.	Inference.
To the filtrate add dil hydrochloric acid.	*H_2S evolved (lead acetate test).	*Sulphide* present.
	*SO_2 evolved (bichromate paper test). Solution clear.	*Sulphite* present.
	*SO_2 evolved Yellow precipitate of sulphur	*Thiosulphate* present.
Boil the filtrate with dil hydrochloric acid till all CO_2 has been given off Add barium chloride	White precipitate insoluble in hydrochloric acid.	*Sulphate* present.

* The CO_2 evolved simultaneously with H_2S or SO_2 does not affect the tests for H_2S or SO_2

Sulphuric Acid

Commercial sulphuric acid, or "oil of vitriol," may contain certain impurities.

Specimens of impure acid are put on the demonstrator's table. Test them as described below for the impurities named.

When diluting sulphuric acid always *add the acid to the water*—not *vice versa.*

Use small quantities

EXPT. 151.—(*a*) **Test for the presence of sulphur dioxide.**—Dilute a little of the acid.

Add a few drops of a freshly prepared solution of potassium ferricyanide, $K_3Fe(CN)_6$. Add a few drops of ferric chloride. A blue coloration (Prussian blue) indicates the presence of *sulphur dioxide.*

EXPLANATION.—The sulphur dioxide reduces the potassium ferricyanide to ferrocyanide. The potassium ferrocyanide reacts with ferric chloride to give Prussian blue.

$$\underset{\text{Potassium ferrocyanide}}{3K_4Fe(CN)_6} + 4FeCl_3 = \underset{\text{Prussian blue}}{Fe_4(Fe(CN)_6)_3} + 12KCl$$

(*b*) **Test for the presence of oxides of nitrogen.**—Add the concentrated acid to a freshly prepared solution of ferrous sulphate as in the test for a nitrate (Expt. 101, page 104). A black ring or black coloration indicates the presence of *oxides of nitrogen.*

(*c*) **Test for the presence of iron.**—Dilute a little of the acid (five times). Add dilute potassium ferrocyanide solution. A blue or green coloration indicates the presence of *iron* in the acid.

(*d*) **Test for the presence of lead sulphate.**—Dilute the acid and let it stand. A white cloudiness or precipitate indicates the presence of *lead sulphate.* If no precipitate appears add alcohol. If the solution remains clear on standing *lead sulphate is absent.* The precipitate should be soluble in a solution of ammonium acetate.

(*e*) **Test for the presence of arsenic.**—The demonstrator will show you Marsh's test.

An apparatus for generating hydrogen is set up and, when the gas is coming off in the pure state, the jet is ignited. A cold, white vessel is depressed into the flame. If no black deposit forms the hydrogen is free from arsenic (or antimony). Blow out the flame. Pour some of the acid in the Woulfe's bottle through the thistle funnel. When the gas is pure (test) light the jet again. Once more depress the cold porcelain in the flame. If a black film, soluble in sodium hypochlorite, is deposited on the porcelain *arsenic was present* in the given sample of sulphuric acid.

Draw a diagram of the apparatus in your note-book.

Sodium hypochlorite is made when required by adding chlorine water to cold sodium hydrate solution.

$$2NaOH + Cl_2 = \underset{\substack{\text{Sodium}\\\text{hypochlorite}}}{NaOCl} + H_2O + NaCl.$$

DEMONSTRATION 32

TESTS FOR ACIDS—*continued*

The Halogen Acids

Write equations representing the reactions which take place. The correct equations will be found at the end of the demonstration.

EXPT. 152.—**Test of hydrochloric acid,** HCl.

Use sodium chloride, $NaCl$.

1. To a solution of the salt in water add silver nitrate ($AgNO_3$) solution. A *white* curdy precipitate of silver chloride comes down. The precipitate is insoluble in strong hot nitric acid. It is soluble in ammonium hydrate, $NH_4{\cdot}OH$.

2. Mix some sodium chloride with a little manganese dioxide, MnO_2, and put it in a test-tube. Add sulphuric acid. Chlorine is given off. Test the chlorine (1) by its odour, (2) by its action on potassium-iodide-starch paper (blue coloration).

(3) When strong sulphuric acid acts on a chloride, hydrochloric acid gas (HCl) is evolved. It fumes in air. With ammonia it gives dense white fumes of ammonium chloride (NH_4Cl).

EXPT. 153.—**Hydrobromic acid,** HBr.

Use sodium, $NaBr$, or potassium bromide, KBr.

1. To the solution of potassium bromide add silver nitrate solution ($AgNO_3$). A *yellowish-white* precipitate of silver bromide ($AgBr$) is produced. It is sparingly soluble in ammonium hydrate, insoluble in nitric acid.

2. Mix some bromide with a little manganese dioxide (MnO_2) and put it in a test-tube. Add strong sulphuric acid (H_2SO_4) and warm. Dense and suffocating *brown* fumes of bromine are

evolved. If these fumes are passed into ferrous sulphate solution *no black coloration is produced* (distinction from nitrogen dioxide). Starch paper is coloured *yellow.*

3. To a bromide add strong sulphuric acid. Dense *white fumes* are given off which give a *white cloud* with ammonia. The fumes will probably be contaminated with bromine.

4. To a solution of a bromide add chlorine water and carbon disulphide. Shake up the mixture. The chlorine releases bromine from the potassium bromide and this free bromine dissolves in carbon disulphide, giving a *yellow or brown* solution, which sinks to the bottom of the tube owing to the insolubility of carbon disulphide in water.

EXPT. 154.—**Hydriodic acid,** HI.

Use potassium iodide, KI.

1. To a solution of potassium iodide add silver nitrate ($AgNO_3$) solution. A *yellow* precipitate of silver iodide (AgI) comes down. It is insoluble in nitric acid (HNO_3) and practically insoluble in ammonium hydrate.

2. Mix some of the iodide with manganese dioxide and put the mixture in a test-tube. Pour strong sulphuric acid on the mixture and warm. Violet-coloured vapours of iodine are evolved. The iodine will condense on the cool parts of the tube as a black or greyish-black solid. The vapour of iodine turns moist starch paper blue.

3. If an iodide is treated with strong sulphuric acid, hydriodic acid mixed with iodine is given off.

4. To a solution of an iodide add chlorine water and carbon disulphide. Shake up the mixture. The chlorine releases iodine from the potassium iodide. The iodine dissolves in carbon disulphide, forming a fine violet solution which sinks to the bottom of the tube owing to the insolubility of carbon disulphide in water.

5. To a solution of potassium iodide add a solution of mercuric chloride ($HgCl_2$). A yellow precipitate which changes to a red colour is produced. It is soluble in excess of either reagent.

EXPT. 155.—**Hydrofluoric acid,** HF.

Use any fluoride. Say calcium fluoride, CaF_2.

1. Silver nitrate gives no precipitate with a solution of a fluoride because silver fluoride is soluble in water.

2. When a fluoride is treated with strong sulphuric acid, hydrofluoric acid is evolved. This attacks the glass of the tube by dissolving silica.

If the upper part of the tube is seen to become etched it may be assumed that hydrofluoric acid is present. To confirm this mix some calcium fluoride with some sand or silica in a small leaden capsule. To the mixture add strong sulphuric acid. Silicon tetrafluoride (SiF_4) is evolved. In the vapour hold a glass tube on the end of which is hanging a drop of water. The silicon tetrafluoride attacks the water, giving **a gelatinous mass of silicic acid** (H_2SiO_3) which hangs as a blob on the end of the glass rod.

EXPT. 156.—**Chloric acid,** $HClO_3$.

Use potassium chlorate, $KClO_3$.

1. Heat small quantity of the substance in a test-tube—oxygen is evolved.

2. Take a *very small quantity* of the salt and put it in a test-tube. Pour a *small quantity* of strong sulphuric acid on it. Warm very gently. A series of explosions takes place in the test-tube. This reaction is characteristic of chlorates.

Equations

Hydrochloric Acid

1.	$NaCl$	$+$	$AgNO_3$	$=$	$AgCl$	$+$	$NaNO_3$
	Sodium chloride	and	Silver nitrate	give	Silver chloride	and	Sodium nitrate

2.	MnO_2	$+$	$2NaCl$	$+$	$3H_2SO_4$	$=$
	Manganese dioxide	and	Sodium chloride	and	Sulphuric acid	give

$2NaHSO_4$	$+$	Cl_2	$+$	$MnSO_4$	$+$	$2H_2O$
Sodium bisulphate		Chlorine		Manganese sulphate		Water

$2KI$	$+$	Cl_2	$=$	$2KCl$	$+$	I_2
Potassium iodide	and	Chlorine	give	Potassium chloride	and	Iodine (blue colour with starch)

3.	$NaCl$	+	H_2SO_4	=	$NaHSO_4$	+	HCl
	Sodium chloride	and	Sulphuric acid	give	Sodium bisulphate	and	Hydrochloric acid

HCl	+	NH_3	=	NH_4Cl
Hydrochloric acid	and	Ammonia	give	Ammonium chloride

Hydrobromic Acid

1, 2, 3 as for hydrochloric acid.

4.	$2KBr$	+	Cl_2	=	$2KCl$	+	Br_2
	Potassium bromide	and	Chlorine	give	Potassium chloride	and	Bromine

Hydriodic Acid

1, 2, 3, 4 as for hydrochloric or hydrobromic acid.

5.	$HgCl_2$	+	$2KI$	=	HgI_2	+	$2KCl$
	Mercuric chloride	with	Potassium iodide	gives	Mercuric iodide (red precipitate)	and	Potassium chloride

Hydrofluoric Acid

2.	CaF_2	+	H_2SO_4	=	$CaSO_4$	+	$2HF$
	Calcium fluoride	with	strong Sulphuric acid	gives	Calcium sulphate	and	Hydrofluoric acid

$4HF$	+	SiO_2	=	SiF_4	+	$2H_2O$
Hydrofluoric acid	and	Silica	give	Silicon tetrafluoride	and	Water

$3SiF_4$	+	$3H_2O$	=	$2H_2SiF_6$	+	H_2SiO_3
Silicon tetrafluoride	with	excess of Water	gives	Hydrofluosilicic acid	and	Silicic acid

Chloric Acid

2.	$3KClO_3$	+	$2H_2SO_4$	=	$KClO_4$	+	$2KHSO_4$	+	$2ClO_2$	+	H_2O
	Potassium chlorate	heated with	strong sulphuric acid	gives	Potassium perchloride		Potassium bisulphate		Chlorine peroxide	and	Water

$2ClO_2$			Cl_2	+	$2O_2$
Chlorine peroxide	with water	give with explosion	Chlorine	and	Oxygen

DEMONSTRATION 33

TESTS FOR ACIDS—*continued*

EXPT. 157.—**Boric acid,** H_3BO_3

Use borax, $Na_2B_4O_7$.

1. Heat a borate on a platinum wire. Borates usually swell up (intumesce) at first and then settle down into a transparent bead. They colour the clear Bunsen flame green unless some other colour masks it.

2. Put some borax into a crucible or into a piece of broken porcelain. Mix with some strong sulphuric acid and pour some methylated spirit over it. Now ignite the methylated spirit. The spirit burns with a bright green edged flame. The colour appears more intense if the mixture is stirred while it is burning.

3. Dip a piece of turmeric paper into a solution of borax which has been made acid with hydrochloric acid. Dry the paper by laying it on the outside of a tube filled with hot water. The paper turns a reddish-brown colour. On treatment with caustic soda solution the reddish-brown colour changes to a bluish-black.

EXPT. 158.—**Acetic acid,** $CH_3{\cdot}COOH$.

Use sodium acetate, $CH_3{\cdot}COONa$.

Write equations where possible.

1. All acetates when heated give inflammable gases which burn, giving carbon dioxide and steam. The residue is usually a carbonate and, if the carbonate is decomposed by heat, an oxide. In some cases a residue of a metal may be left, *e.g.*, heat some copper acetate in a tube. A yellowish-red residue of metallic copper will be found in the tube.

2. When an acetate is treated with a little 50 per cent. sulphuric

acid, vapours are given off which smell like vinegar. This is due to free acetic acid ($CH_3 \cdot COOH$).

3. To a solution of an acetate add ferric chloride solution. A red coloration, due to the presence of ferric acetate, is produced. When the solution is boiled basic ferric acetate separates as a reddish precipitate. The red coloration, due to ferric acetate, is destroyed by dilute hydrochloric acid.

EXPT. 159.—**Phosphoric acid,** H_3PO_4.

Use sodium hydrogen phosphate Na_2HPO_4.

Write equations where possible.

1. To a solution of sodium hydrogen phosphate add silver nitrate solution. A yellow precipitate of silver phosphate (soluble in ammonium hydrate and in nitric acid) is precipitated.

2. To a solution of a phosphate add ammonium chloride, NH_4Cl, solution. Boil, cool, and add ammonium hydrate ($NH_4 \cdot OH$). To this add magnesium sulphate ($MgSO_4$) solution. Warm and shake up the tube. A crystalline precipitate of magnesium ammonium phosphate comes down.

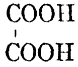
3. To a solution of the phosphate add nitric acid and heat. Heat a solution of ammonium molybdate ($(NH_4) \cdot HMoO_4$) with nitric acid. Now mix these two solutions and heat again. A yellow precipitate indicates the presence of a phosphate. If the precipitate does not form at once stand the tube on one side. The precipitate should form after some time.

EXPT. 160.—**Silica,** SiO_2.

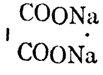
Silica is the "acid oxide" of silicic acid. Use common sand.

1. Silica is insoluble in the mineral acids. It is infusible.

2. Mix some silica with calcium fluoride and pour upon it some strong sulphuric acid. Heat the mixture in a leaden capsule and, hanging a drop of water on a glass rod, hold it in the vapour. The formation of a gelatinous blob on the end of the rod shows that silica was present (*vide* Hydrofluoric acid, Expt. 155 (2), page 140).

EXPT. 160 (*a*).—**Oxalic acid,** 

$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$

Use sodium oxalate, 

$\begin{array}{l}\mathrm{COONa}\\ |\\ \mathrm{COONa}\end{array}$

NOTES ON SYSTEMATIC EXAMINATION OF GASES

NOTE No. 1.—**To detect sulphuretted hydrogen and carbon dioxide in the presence of each other.**—Shake the gas up with a suspension of cadmium carbonate or lead carbonate in water.

If, with cadmium carbonate, the suspension turns yellow (owing to the formation of cadmium sulphide, CdS), or, with lead carbonate, the suspension turns black (owing to the formation of lead sulphide), the presence of *sulphuretted hydrogen* is indicated. The presence of sulphuretted hydrogen does not affect the lime-water test for carbon dioxide (*vide* Expt. 136, page 125).

NOTE No. 2.—**To detect carbon dioxide, sulphur dioxide and carbon monoxide in the presence of each other.**—Pass the gas through—

(A) A weak solution of potassium dichromate acidified with hydrochloric acid. If the colour of the solution is changed from yellow to green, *sulphur dioxide* is present (Expts. 141 and 142, pages 130 and 131).

(B) Lime-water. If the lime-water is turned milky the presence of carbon dioxide is indicated.

Try to ignite the remaining gas as it issues at C (Fig. 66). If it burns with a pale blue flame, forming carbon dioxide, then the presence of carbon monoxide is indicated. Confirm this by showing that the gas is soluble in a solution of cuprous chloride in ammonium hydrate.

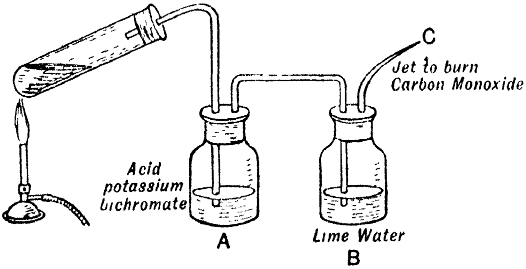


FIG. 66

DEMONSTRATION 34

SYSTEMATIC EXAMINATION OF GASES

EXPT. 161.—**Identification of Gases.**

Perform the following Experiments upon each of the given substances :—

(1) Heat alone in a test-tube
(2) Heat with dilute sulphuric acid
(3) Heat with strong sulphuric acid.

Identify the gas or gases given off by the help of this table.

The gases treated of in the scheme are as follows—Cl_2, ClO_2, Br_2, I_2, NO_2, N_2O, NO, NH_3, N_2, H_2S, SO_2, SO_3, CO, CO_2, C_2H_2, CH_4, (HCl, HBr, HI, HNO_3, CH_3COOH).

They can be divided into three classes, (1) Coloured gases, (2) Colourless gases, (*a*) having a distinct smell, (*b*) having no smell

THE GAS IS COLOURED.	THE GAS IS COLOURLESS.			
	IT HAS AN ODOUR	NO DISTINCT ODOUR CAN BE DETECTED		
		IT SUPPORTS COMBUSTION	IT BURNS	IT NEITHER BURNS NOR SUPPORTS COMBUSTION.
Yellow. Explosions in the tube. Gas is CHLORINE PEROXIDE and indicates the presence of a CHLORATE **Yellowish-green.** Characteristic odour Turns potassium iodide starch paper blue It is CHLORINE **Brown.** 1. Pass gas into a solution of ferrous sulphate solution. It is turned black. It is NITROGEN PEROXIDE 2. Pass gas into water (*a*) solution gives tests for nitrous and nitric acids It is NITROGEN PEROXIDE (*b*) Solution is brownish Shake with carbon disulphide The disulphide turns brown It is BROMINE **Violet.** 1 Dissolves in carbon disulphide to a violet solution (2) turns starch paper blue It is IODINE. **White** may be SULPHUR TRIOXIDE ; passed into water gives tests for sulphates **Other Coloured Vapours** may be certain salts etc and will be discussed later.	1 Characteristic smell of ammonia Turns red litmus paper blue, and turmeric paper brown It is AMMONIA 2 Smell like rotten eggs Turns moist lead acetate paper black— SULPHURETTED HYDROGEN 3. Smell of burning sulphur. Turns a filter paper moistened with an acid solution of potassium bichromate a bluish or green colour It is SULPHUR DIOXIDE 4 Pungent strongly acid irritating fumes They give a white cloud with ammonia May be (1) HYDROCHLORIC ACID, (2) possibly accompanied by bromine HYDROBROMIC ACID, (3) possibly accompanied by iodine HYDRIODIC ACID (4) accompanied by oxides of nitrogen NITRIC ACID 5 Smell of vinegar— ACETIC ACID 6 Peculiar smell of ACETYLENE Gas burns with a smoky flame, giving carbon dioxide and steam Shake with a solution of cuprous chloride in ammonia, a reddish-brown precipitate indicates ACETYLENE 7 CHLORINE may be detected here 8 CO_2, CO, and N_2O. Smell not sufficiently characteristic.	It may be OXYGEN OR NITROUS OXIDE Boil the original substance with sodium hydrate if ammonia is evolved the gas is probably NITROUS OXIDE from ammonium nitrate Confirm by mixing the gas with nitric oxide (NO) The mixture goes brown the gas is OXYGEN There is no brown coloration Gas is NITROUS OXIDE	1 Flame is colourless or nearly colourless no carbon dioxide is produced It is HYDROGEN 2 Flame is pale blue Carbon dioxide but no water is produced The gas is soluble in a solution of cuprous chloride in ammonia or in hydrochloric acid No precipitate is formed in solution Gas is CARBON MONOXIDE 3 Flame is luminous and smoky Water and carbon dioxide are formed Shake up the gas with a solution of cuprous chloride in ammonium hydrate A reddish-brown precipitate indicates presence of ACETYLENE 4 Flame is luminous but not smoky Carbon dioxide and water are formed Gas is not soluble in acid or ammoniacal solution of cuprous chloride Gas is possibly MARSH GAS 5. Many organic substances give inflammable vapours on heating, *e g*, acetates	It turns brown on exposure to air It is NITRIC OXIDE It turns lime-wate milky It is CARBON DIOXIDE It gives none o the foregoing tests It is NITROGEN.

Revise the tests given in Demonstration 20, Expt. 84, page 90. *For the systematic separation of acids see page* 134 *et seq.*

Equations

Acetic Acid

(1)	$2CH_3\cdot COONa$	$=$	Na_2CO_3	$+$	$CH_3\cdot CO\cdot CH_3$, etc., etc.
	Sodium acetate		Sodium carbonate		Acetone (inflammable)

(2)	$CH_3\cdot COONa$	$+$	H_2SO_4	$=$	$CH_3\cdot COOH$	$+$	$NaHSO_4$
	Sodium acetate	with	Sulphuric acid	gives	Acetic acid	and	Sodium bisulphate

(3)	$3CH_3\cdot COONa$	$+$	$FeCl_3$	$=$	$(CH_3\cdot COO)_3Fe$	$+$	$3NaCl$
	Sodium acetate	with	Ferric chloride	gives	Ferric acetate (red coloration)	and	Sodium chloride

$(CH_3\cdot COO)_3Fe$	$+$	$3HCl$	$=$	$3(CH_3\cdot COOH)$	$+$	$FeCl_3$
Ferric acetate	and	Hydrochloric acid	give	Acetic acid	and	Ferric chloride

Phosphoric Acid

1.	Na_2HPO_4	$+$	$AgNO_3$	$=$	Ag_3PO_4	$+$	$2NaNO_3$	$+$	HNO_3
	Disodium hydrogen phosphate		Silver nitrate		Silver phosphate		Sodium nitrate		Nitric acid

2.	Na_2HPO_4	$+$	$NH_4\cdot OH$	$+$	$MgSO_4$	
	Disodium hydrogen phosphate		Ammonium hydrate		Magnesium sulphate	
$=$	$Mg(NH_4)PO_4$	$+$	H_2O	$+$	Na_2SO_4	
	Magnesium ammonium phosphate		Water		Sodium sulphate	

Silica

See explanation and equations in demonstration on hydrofluoric acid, pages 139 and 140.

DEMONSTRATION 35

SYSTEMATIC EXAMINATION FOR ACID RADICALS

EXPT. 162.—**Test the given substances and find what acid radical is present in each.**—The acid radicals of the following classes of salts may be detected by the tables given below.

Arsenates, borates, fluorides, chlorides, bromides, iodides, sulphides, sulphites, sulphates, thiosulphates, nitrates, nitrites, carbonates, bicarbonates, acetates, oxalates, phosphates, and silicates.

In all cases confirm the tests by those given under the headings of the acids separately.

I.—Heat a little of the substance dry in a small test-tube.

OBSERVATION.	INFERENCE.
1. Water vapour is given off and condenses on the upper part of the tube.	Water of crystallisation or water from an acid salt
2 Substance swells up (intumescence)	Alums, borates, phosphates.
3 There is a sublimate on the upper part of the tube.	Sulphur (smell of sulphur dioxide) — certain sulphides Some coloured salts, *e g.*, mercuric iodide.
It is white—smell of ammonia.	Certain ammonium salts
It is black—with purple vapour.	Iodine from certain iodides.
4 A gas is given out—	
(*a*) *It is coloured* Yellowish. Distinct smell (KI and starch paper).	Chlorine from some hypochlorite.
Brown (iron sulphate solution blackened).	Oxides of nitrogen from nitrates.
White (very pungent and acid).	Sulphur trioxide from certain sulphates.
(*b*) *Colourless*, but has distinct smell—	
Rotten eggs (lead acetate paper).	Sulphuretted hydrogen from thiosulphates
Sulphur dioxide (potassium chromate paper).	Some sulphides, sulphites, thiosulphates and bisulphites.
Sulphur dioxide and sulphuretted hydrogen	Thiosulphates
Ammonia.	Ammonium salts.

OBSERVATION.	INFERENCE.
(*c*) *Colourless and odourless.*	
1. The gas burns.	Carbon monoxide from oxalates.
Organic fumes which burn	Acetates.
2 The gas supports combustion.	Oxygen from nitrates, chlorates, peroxides.
Supports combustion and gives no coloration with nitric oxide	Ammonium nitrate present (test for ammonia and NO_3 at once)
3 Gas neither burns nor supports combustion	Carbon dioxide, carbonates, bicarbonates (some oxalates and acetates).
4 Gas fails all the above tests	Nitrogen from ammonium nitrite

II.—**Treat substance with dilute acid** (HCl or H_2SO_4).

OBSERVATION	INFERENCE.
A gas is evolved—	
Coloured Yellowish-green (KI starch paper).	Chlorine from hypochlorite, chlorate, peroxide.
Brown (turns ferrous sulphate solution black)	Nitrite present (confirm).
Colourless, but has odour—	
Rotten eggs (turns lead acetate paper black).	Sulphuretted hydrogen from most sulphides.
Smell of burning sulphur (SO_2)	Sulphite or bisulphite.
Yellow sulphur separates as well as evolution of sulphur dioxide	Thiosulphate (confirm).
Colourless and odourless	
Turns lime-water milky (CO_2).	From carbonate or bicarbonate

NOTE.—If the substance is a bicarbonate it will be soluble in water. On heating it will give carbon dioxide and water vapour. To a solution of the salt add a solution of magnesium sulphate. No precipitate is produced in the cold, but on warming a precipitate of magnesium carbonate is thrown down and carbon dioxide is evolved.

III.—Treat a little of the original substance with cold concentrated sulphuric acid. Warm very cautiously.

OBSERVATION.	INFERENCE.
A series of explosions takes place.	Chlorate present.
A gas is evolved	
Brown (turns ferrous sulphate black).	Nitrate or nitrite.
Brown } accompanied by dense acid fumes.	Bromine from bromide.
Violet }	Iodine from iodide.
White—dense acid fumes giving dense white fumes with ammonia.	Hydrochloric acid gas from a chloride, or
White fumes, strongly acid in reaction	Possibly due to overheating your sulphuric acid.
Fumes which corrode glass.	Fluoride.
If chloride, bromide or iodide is suspected, mix some of the substance with manganese dioxide and warm the mixture with strong sulphuric acid.	
Chlorine is evolved (yellowish-green)	Chloride is present.
Bromine is evolved (brown).	Bromide is present.
Iodine is evolved (violet).	Iodide is present.

IV.—Test separately for borate, fluoride, or silicate.

EXPERIMENT AND OBSERVATION.	INFERENCE.
(*a*) Put a little of the original substance on porcelain Pour strong sulphuric acid on it and mix well Pour alcohol on the mixture. Ignite the alcohol. Stir the mixture when the alcohol is burning. It burns with a green flame.	Borate present
(*b*) Mix some of the substance with a little sand. Pour sulphuric acid on the mixture and warm gently. Dip a glass rod in water and plunge the rod into the mouth of the tube. A gelatinous blob forms on the end of the rod (*vide* page 140).	Fluoride present.
(*c*) Mix some of the substance with calcium fluoride and put it in a leaden capsule. Pour strong sulphuric acid on the mixture and warm. Suspend a drop of water on a watch-glass and cover the capsule with it. A gelatinous blob forms on the watch-glass where the drop of water was (*vide* page 143).	Silica or a silicate present.

So far we have no indication of phosphate, arsenate or sulphate. They are easily detected by the "wet" analysis given below.

EXPT. 163.—**Wet tests for acids.**

1. Dissolve some of the substance in water and add sodium carbonate solution. If no precipitate is formed use a solution of the original substance for the following tests.

2. If a precipitate is formed on the addition of sodium carbonate, filter the solution and use the filtrate for the following tests.

3. If the substance is insoluble in water mix it with about four or five times its weight of sodium carbonate. Add water in about sufficient quantity to dissolve the sodium carbonate and boil the mixture for some time. (You may use a saturated solution of sodium carbonate.) Take care that the solution does not "bump" over. Filter, and divide the filtrate into five portions, I–V.

No. I.—Neutralise the excess of sodium carbonate with dilute hydrochloric acid. Warm to drive off carbon dioxide.

White precipitate insoluble in all acids (except hydrofluoric). Silica indicating the presence of a SILICATE. Be sure the white precipitate is not sulphur from a thiosulphate.	Solution clear. Add barium chloride solution. White precipitate insoluble in acids and insoluble on diluting with water indicates the presence of a SULPHATE.

No. II.—Neutralise the excess of sodium carbonate with dilute nitric acid. Boil off carbon dioxide and add silver nitrate solution.

(1) A white precipitate, soluble in ammonium hydrate, reprecipitated on adding dilute nitric acid CHLORIDE present.	Pale yellow precipitate sparingly soluble in ammonium hydrate, insoluble in dilute nitric acid, indicates the presence of a BROMIDE.	Yellow precipitate insoluble in ammonium hydrate and dilute nitric acid indicates the presence of an IODIDE.

NOTE.—If bromide or iodide is suspected (1) Heat the original substance with manganese dioxide and sulphuric acid. Brown fumes of bromine indicate a bromide. Violet fumes of iodine indicate an iodide.

(2) Treat some of the rest of the solution, neutralised with

dilute nitric acid, with chlorine water. Shake up with carbon disulphide. A brown coloration in the carbon disulphide indicates a bromide. A violet coloration in the carbon disulphide indicates an iodide.

No. III.—If chloride, bromide and iodide are absent neutralise with dilute nitric acid; boil off all gases. Add ammonium hydrate and boil till neutral; add silver nitrate solution.

White precipitate may be oxalate, etc; reject. See below.	Canary yellow precipitate indicates PHOSPHATE. Boil a portion of remaining solution with nitric acid. Boil some ammonium molybdate solution with nitric acid. Mix the solutions. Boil. A canary yellow precipitate confirms a PHOSPHATE.	Orange-coloured precipitate probably a SILICATE Confirm by Test No. 2, Expt. 160, on page 143.	Reddish-brown precipitate probably an ARSENATE Take some of solution Pass sulphur dioxide into it. Warm to drive off excess of sulphur dioxide. Pass sulphuretted hydrogen A canary yellow precipitate insoluble in hot strong hydrochloric acid confirms an ARSENATE.	Yellow precipitate probably an ARSENITE. Prove phosphate absent. A neutral solution of an arsenite will bleach a solution of iodine in potassium iodide Arsenites give a yellow precipitate with sulphuretted hydrogen without previous reduction with sulphurous acid.

No. IV.—Neutralise the excess of sodium carbonate with dilute sulphuric acid. Boil off all gases. Cool. Add a freshly prepared solution of ferrous sulphate and then strong sulphuric acid by allowing it to flow gently down the tube.

A black layer or ring at the point of separation of the sulphuric acid layer indicates the presence of a

NITRATE

No. V.—Neutralise the excess of sodium carbonate with acetic acid. Divide the solution into two parts.

1. Add calcium chloride solution. A white precipitate soluble in dilute hydrochloric and nitric acids indicates an OXALATE. Confirm by tests on page 90.	2. Add ferric chloride. Yellowish-white precipitate indicates PHOSPHATE Confirm by the ammonium molybdate test.

DEMONSTRATION 36

REACTIONS OF THE COMMONER METALS

PRELIMINARY DEMONSTRATION

1. EXPT. 164.—**Describe your substance carefully.**—See if you can draw any inferences from the external appearance of the body.

The object of this demonstration is to give you practice in the ordinary processes, to which you must submit the substances given to you for examination. Each process is very important, and you should take pains to get proficient in its manner of manipulation. Be sure you have carried out all instructions carefully before condemning a test as unsuccessful or unreliable.

2. EXPT. 165.—**Action of heat alone on the substance.**—It is most important to notice *all* that happens, and the most valuable conclusions may be arrived at by allowing the reaction under consideration to proceed to its completion. This cannot be done if large masses of material are used. It is difficult to heat them throughout, and, moreover, when the reaction is being completed in one portion of the mass it is only starting in the other, hence it is difficult to form an opinion as to what *is happening* or what *has already happened.* The first rule then is—

USE SMALL QUANTITIES.

Divide your observations broadly into four classes :

1. What happens *during the heating* such as melting, decrepitation, changes of colour, etc.
2. What *gases or vapours* are given off. You have already been given a scheme by which these may be identified (Expt. 161, pages 145 and 146).
3. What *condenses* on the upper part of the tube.
4. The nature and properties of the *residue.*

Write your results in tabular form, and in your descriptions always use the *first person singular.*

Use three columns.

In the first write down exactly what you do: "Experiment." In the second write down all that you observe with your senses —sight, smell, etc.: "Observation." In the third write down the conclusions at which you arrive as the result of your observations: "Inference."

Thus—

EXPERIMENT.	OBSERVATION.	INFERENCE.
I treated the given substance with dilute hydrochloric acid in a test-tube.	Effervescence took place. A gas was evolved. It was colourless and odourless.	∴ Cl, Br, etc, absent. ∴ SO_2, H_2S, etc., absent.
I applied a lighted match to the mouth of the test-tube.	The match was extinguished. The gas did not burn.	∴ N_2O and O_2 absent. ∴ H_2, CO, C_2H_2, CH_4 absent. May be CO_2 or N_2.
I passed the gas into lime-water.	The lime-water was turned milky.	The gas is CARBON DIOXIDE

Heat the given substances *C, D* in a bulb-tube, and write down all you observe and the inferences you come to. Tabulate your results.

3. EXPT. 166.—**Action of dilute hydrochloric acid.**—Treat the given substances *E, F* with dilute hydrochloric acid. Tabulate your observations and inferences. Try action of dilute sulphuric acid also.

4. EXPT. 167.—**Action of strong sulphuric acid.**—Heat the given substances *G, H* with strong sulphuric acid. Tabulate your observations and inferences.

5. **Use of the mouth blow-pipe.**—To do this a continuous blast must be maintained. In order to do this you must use the contraction of your cheeks to expel the air from your mouth into the blow-pipe, and breathe through your nose. Keep the cheeks more or less distended, and use the tongue to force the air from the mouth in combination with the partial contraction of the cheeks. The ability to produce a steady blast will not come at once, but practice and patience will enable you to acquire ease in the use of the blow-pipe. Do not try to blow hard—a gentle blast is sufficient. Use a small slot in the blow-pipe, or shut the air-holes at the base of the burner, and use the luminous flame so produced. Do not attempt to use a large flame. Direct the blast across the mouth of the

burner, not *down* the burner, or the flame will be extinguished. If you have any difficulty in holding the blow-pipe steady, rest it on the side of the orifice of the burner.

Notice the flame which is produced.

The inner portion is the reducing flame.

The outer portion is the oxidising flame.

The parts are shown in Fig. 4, page 7.

6. Expt. 168.—**Heat J, mixed with sodium carbonate on charcoal under the blow-pipe.**—Mix some of the substance *J* with sodium carbonate. Make a small cavity in a piece of charcoal and put a little of the mixture in the cavity. Now heat it in the blow-pipe flame. Write down all you see. If a metallic bead is produced cut it out of the charcoal and gently grind it in a mortar containing some water. The carbon will be easily washed away. Examine the metal which is left after the light matter has been washed away. Write down its properties.

Note if there are any fumes given off when you are heating.

See if there is an incrustation on the charcoal. Look out for decrepitation, deflagration, etc.

If you get a white residue moisten it with two drops of cobalt chloride or cobalt nitrate and heat it again ; note any colour change.

N.B.—Do not attempt to get " oxidation " results on charcoal.

Borax bead tests.—When borax is heated it swells up (intumesces) and eventually solidifies to a glassy mass. This glassy mass will dissolve the oxides of certain metals with the formation of coloured beads. Microcosmic salt (sodium ammonium hydrogen phosphate), $Na(NH_4)HPO_4,4H_2O$, may be used in the place of borax. In this case the oxides of metals dissolve forming double phosphates. The colour of the bead with a given metal is the same in each kind of bead (*i.e.*, borate or phosphate). The colour of the bead for a given metal after heating in the oxidising flame is often different from the colour of the bead for the same metal after heating in the reducing flame.

The blow-pipe flame may be used for making the borax bead, but the clear Bunsen flame may be used as well.

Expt. 169.—**To make a borax bead.**—Make a circular loop at the end of your platinum wire about this size ○ (wind the wire 1½ times round the point of your pencil). Heat the ring in the clear

Bunsen or the blow-pipe flame and then dip it in powdered borax. Heat again and repeat the process, taking more borax on to the wire until it has the loop filled with *a clear lens-shaped bead.* If you try to put too much borax on to the loop the bead will not stay on the wire. Dip the bead into the substance *K* which it is desired to test. *Only take a minute quantity of K;* if you take too much the bead will become opaque.

Find what coloured bead you get (1) in the oxidising, (2) the reducing flame.

The colours produced are—

IN THE INNER OR REDUCING FLAME.	IN THE OUTER OR OXIDISING FLAME.	INDICATES THE PRESENCE OF
Red when cold (addition of tin helps the results).	Green when hot Blue when cold.	Copper
Yellowish when hot. Olive green when cold.	Brownish-red when hot Light yellow when cold.	Iron.
Green.	Green.	Chromium
Blue	Blue.	Cobalt.
Grey or opaque and black	Cherry red when hot. Brownish when cold.	Nickel.
Colourless.	Amethyst (violet).	Manganese
Opaque.	Opaque.	Too much substance; start again.
White	White.	Many substances.
White skeleton floating in bead.	White skeleton floating in bead.	Silica.

To clean the wire heat it and then shake off the molten bead. Further washing may be done by fusing borax on to the wire and shaking it off and repeating this several times. If the wire has to be cleaned for No. 7 (below), dip it in strong hydrochloric acid and heat it in the flame. Repeat this until the flame gives no appreciable yellow coloration when dipped first in hydrochloric acid and then heated in the flame.

7. EXPT. 170.—**To fuse a platinum wire into glass.**—Take a short length of glass tubing. Heat it in the Bunsen flames till it thickens, and then draw it out slighly. Let the tube cool and then cut it at the constriction. Slip the wire in the fine hole and then, holding the wire and the tube, heat the glass at the junction of the wire and the glass. The wire is cleaned as described in the foregoing paragraph.

EXPT. 171.—**Flame coloration.**—Moisten the wire with hydrochloric acid (*not from the bottle direct*—pour a little hydrochloric acid into a watch-glass and use that. Throw it away after using). Do not use the same hydrochloric acid for testing two different substances. Now dip the wire in the given substance and introduce it into the outer zone near the base of the clear Bunsen flame.

The blow-pipe may often be used with advantage for these "flame tests."

All the flames are viewed directly with one exception. When testing for potassium look at the flame through a piece of cobalt blue glass. This cuts out the blue rays and makes the violet flame look red.

Clean the wire after use and keep it in a bottle containing dilute hydrochloric acid.

N.B.—If platinum is not procurable bind a few fibres of asbestos together by an iron wire, and heat the substance moistened with hydrochloric acid on the fibres. Use fresh fibres for each test.

The colours given by various metals are as follows:—

The Colour of the Flame is	Indication.
Brilliant golden-yellow.	Sodium.
Green with (HCl), blue alone.	Copper.
Green.	Borates.
Yellowish-green—very persistent.	Barium.
Violet (looks red through cobalt blue glass).	Potassium.
Crimson—flashes up quickly and does not persist	Strontium.
Dull reddish-yellow.	Calcium.
Pale blue flame.	Many substances.
Smell of garlic, wire corroded	Arsenic.

Note to Demonstrators

Any suitable substances may be given for these exercises, but it should be remembered that easily reducible metals corrode the platinum wire and so should be avoided as often as possible in the experiments where platinum is to be used.

DEMONSTRATION 37

TESTS FOR METALS

Try to write the equations representing the reactions marked with an asterisk (*).

You will find the correct equations at the end of the demonstration (page 161).

EXPT. 172.—**Tests for Sodium,** Na.

Use any sodium salt.

Sodium salts give no definite indications when heated on charcoal or in the borax bead.

Sodium salts colour the Bunsen flame a brilliant golden-yellow colour. The colour is very marked and persists for some time. Compare the flame very carefully with that of calcium.

Nearly every substance gives some yellow colour when heated in the Bunsen flame. When sodium is present in any quantity the flame is very intense, and as this is the best test for sodium you must learn to recognise the flame. Neglect a *faint* yellow coloration.

All the common salts of sodium are soluble in water.

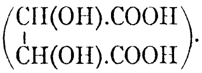
EXPT. 173.—**Tests for Potassium,** K.

Use potassium chloride, KCl.

1. Potassium compounds give no definite indication when heated on charcoal or in the borax bead.

2. Potassium compounds colour the Bunsen flame *violet.* The colour is very easily confused with other bluish colours such as that given by arsenic. Moreover, as traces of sodium are almost invariably present, the bluish colour may be masked by the faint

yellow of the sodium. Look at the flame through a piece of cobalt blue glass. If you see a distinct red colour it is probable that potassium is present. This test should be confirmed in the wet way and is not trustworthy in the presence of substances which give red flames, *e.g.*, calcium or strontium.

*3. Take a strong solution of the salt and see that it is neutral or faintly acid. Add to it a concentrated solution of tartaric acid  $\left(\begin{array}{l}CH(OH).COOH\\ \mid\\ CH(OH).COOH\end{array}\right)$. If the precipitate does not come down, shake the tube violently or stir with a rod. A white, crystalline precipitate of cream of tartar (acid potassium tartrate) indicates the presence of potassium.

*4. To a moderately strong solution of the salt in water add a concentrated solution of picric acid ($C_6H_2(OH)(NO_2)_3$) in water. Let the solution stand. The appearance of long, yellow needles indicates the presence of potassium. Pour this down the sink at once. Ammonium salts must be absent, as ammonium picrate is also precipitated by picric acid.

Most potassium salts are soluble in water.

Expt. 174.—**Tests for Magnesium,** Mg.

Use magnesium sulphate (Epsom salts), $MgSO_4,7H_2O$.

1. Magnesium compounds give no definite indications either by the flame test or the borax bead test.

2. Heat a little of the dry salt on charcoal under the mouth blow-pipe flame. Cool. Put two drops of cobalt nitrate or chloride on the residue and heat again strongly under the blowpipe. The residue becomes a *pink* colour.

Compare with aluminium (page 182), and zinc (page 189).

3. Boil a solution of the substance with ammonium chloride, $(NH_4)Cl$, and add ammonium hydrate $(NH_4)OH$. No precipitate is formed. Add ammonium carbonate, $(NH_4)_2CO_3$, no precipitate is formed. (In the absence of ammonium chloride, precipitates are given with both ammonium hydrate, $(NH_4)OH$, and ammonium carbonate, $(NH_4)_2CO_3$.

*4. Boil the solution with ammonium chloride, $(NH_4)Cl$, cool and add ammonium hydrate, $(NH_4)OH$, and disodium hydrogen phosphate (Na_2HPO_4) solution. If the solution is strong a precipitate of magnesium ammonium phosphate ($Mg(NH_4)PO_4$) comes down at once. If dilute the precipitate will come down on standing, shaking the tube or scratching the inside of the tube. The precipitation is favoured by warming. The precipitate is soluble in dilute mineral acids and acetic acid ($CH_3 \cdot COOH$). Confirm the presence of magnesium in the precipitate by test No. 2 above.

EXPT. 175.—**Tests for Ammonium** (NH_4).—(See page 114.)

Use ammonium chloride, NH_4Cl.

1. Heated in a dry tube some ammonium salts pass into vapour and condense on the upper part of the tube. There are many exceptions, *e.g.*, ammonium nitrate (NH_4NO_3) decomposes into water (H_2O) and nitrous oxide (N_2O), etc. The smell of ammonia gas is often apparent. Many ammonium salts sublime. Ammonia gas turns red litmus paper blue and yellow turmeric paper brown (moisten the paper before applying the test).

*2. To the solid substance add sodium hydrate ($NaOH$) or potassium hydrate (KOH) solution and warm, or mix the dry substances with soda lime and warm if necessary.

Ammonia gas will be evolved.

Test for ammonia by—

(1) Smell.

(2) Red litmus paper.

(3) Turmeric paper.

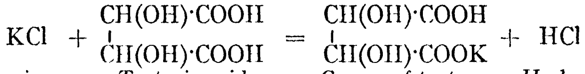
(4) A glass rod dipped in strong hydrochloric acid (HCl) will fume when brought near the mouth of the tube.

(*This test is given by all ammonium salts without any exception.*)

Equations

Potassium

No. 3.



$$\underset{\text{Potassium chloride}}{KCl} \;\underset{\text{with}}{+}\; \underset{\text{Tartaric acid}}{\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array}} \;\underset{\text{gives}}{=}\; \underset{\text{Cream of tartar (white crystalline precipitate)}}{\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOK \end{array}} + \underset{\text{Hydrochloric acid}}{HCl}$$

No. 4. KCl	+	$C_6H_2(NO_2)_3{\cdot}OH$	=	$C_6H_2(NO_2)_3OK$	+	HCl
Potassium chloride	with	Picric acid	gives	Potassium picrate	and	Hydrochloric acid

Magnesium

No. 4. $MgSO_4$	+	Na_2HPO_4	+	NH_4OH	=
Magnesium sulphate	with	Disodium hydrogen phosphate	in presence of	Ammonium hydrate	gives
$Mg(NH_4)PO_4$	+	Na_2SO_4	+	H_2O	
Magnesium ammonium phosphate	and	Sodium sulphate	and	Water	

Ammonium

No. 1.	NH_4Cl	$\rightleftarrows$	NH_3	+	HCl
	Ammonium chloride	heated gives	Ammonia	and	Hydrochloric acid

The reaction is reversible.

$NH_4{\cdot}NO_3$	=	N_2O	+	$2H_2O$
Ammonium nitrate	heated gives	Nitrous oxide gas	and	Steam
$NH_4{\cdot}NO_2$	=	N_2	+	$2H_2O$
Ammonium nitrite	heated gives	Nitrogen gas	and	Steam

No. 2. NH_4Cl	+	$NaOH$	=	NH_3	+	H_2O	+	$NaCl$
Ammonium chloride	with	Sodium hydrate	gives	Ammonia gas,		Water	and	Sodium chloride

DEMONSTRATION 38

TESTS FOR METALS—GROUP I

Try to write the equations representing reactions marked with an asterisk (*). You will find the correct equations at the end of the demonstration (page 167).

EXPT. 176.—**Tests for Silver**, Ag.

Use silver nitrate, $AgNO_3$.

*1. Mix some of the powdered silver salt with sodium carbonate (Na_2CO_3) and heat strongly on charcoal before the blow-pipe. A white bead of silver is obtained. Cut the bead out of the charcoal and put it in a mortar with some water and then press it with the pestle. The carbon floats away and the metal is found to be malleable. It does not mark paper.

2. When silver salts are heated on platinum wire the wire is corroded. Silver gives no characteristic flame or colour to the borax bead.

*3. (*a*) To a solution of a silver salt add hydrochloric acid (HCl). A white, curdy precipitate of silver chloride (AgCl) is formed. The precipitate becomes violet on exposure to light.

(*b*) The precipitate is soluble in ammonium hydrate ($NH_4 \cdot OH$).

(*c*) Add dilute nitric acid (HNO_3) to the ammoniacal solution produced in (*b*). The white precipitate of silver chloride (AgCl) is again formed.

*4. (*a*) To a neutral solution of a silver salt add potassium chromate solution (K_2CrO_4). A dark red precipitate of silver chromate (Ag_2CrO_4) is formed.

(*b*) On the addition of dilute hydrochloric acid (HCl) this precipitate turns white because the red silver chromate (Ag_2CrO_4) is converted to white silver chloride (AgCl).

EXPT. 177.—**Tests for Lead,** Pb.

Use lead nitrate, $Pb(NO_3)_2$.

1. Mix some powdered lead nitrate with some sodium carbonate (Na_2CO_3) and heat it on charcoal under the blow-pipe. The salt will deflagrate. If you do not get a metallic bead easily, mix up some of the salt with a mixture of sodium and potassium carbonates and a little powdered carbon. A metallic bead is formed. It is malleable and will mark paper. A yellow incrustation of lead oxide (PbO) will probably be noticed on the charcoal.

2. Lead salts corrode the platinum wire. They give no characteristic colour to the Bunsen flame or borax bead.

*3. (*a*) To a solution of a lead salt add dilute hydrochloric acid (HCl). A white precipitate of lead chloride ($PbCl_2$) is thrown down.

(*b*) This precipitate ($PbCl_2$) is soluble in hot water, but separates out again in crystals on cooling the solution.

NOTE.—Lead is not completely precipitated by hydrochloric acid.

*4. To a solution of a lead salt add potassium chromate (K_2CrO_4) solution. A yellow precipitate of lead chromate ($PbCrO_4$) is formed which is insoluble in dilute hydrochloric (HCl) and acetic ($CH_3{\cdot}COOH$) acids.

*5. To a solution of a lead salt add dilute sulphuric acid (H_2SO_4). A white precipitate of lead sulphate ($PbSO_4$) is formed. In dilute solutions the precipitate may form slowly. The precipitate comes down more readily when alcohol is added to the solution. Lead sulphate is soluble in ammonium acetate ($CH_3{\cdot}COONH_4$).

*6. Pass sulphuretted hydrogen (H_2S) through a solution of a lead salt made acid by dilute hydrochloric acid (HCl). A black precipitate of lead sulphide (PbS) is thrown down. This precipitate is soluble in 50 per cent. nitric acid, forming lead nitrate.

EXPT. 178.—**Tests for Mercury,** Hg.

There are two classes of mercury compounds—

(1) Those in which mercury behaves as a monovalent metal, called " mercurous " salts.

(2) Those in which mercury behaves as a divalent metal, called " mercuric " salts.

The following reactions (1, 2, 3) are obtained with both "mercurous" *and* "mercuric" salts.

1. Mix the dry compound of mercury with *dry* anhydrous sodium carbonate (Na_2CO_3) and a little dry potassium nitrate and heat the mixture in a small bulb-tube. A deposit of mercury is formed on the upper part of the tube. This deposit may be made to run into small globules by rubbing with a match-stick. Mercury is the only metal which runs into globules under these conditions. Most mercury compounds sublime when heated in a tube.

2. Mercury compounds give no very characteristic reactions when heated on charcoal, neither do they give a characteristic colour to the Bunsen flame or the borax bead.

*3. Add dilute nitric acid to a solution of a mercury salt. Boil with a small piece of clean copper. Mercury will separate on the copper as a white deposit. The solution will turn blue or green. Take the copper from the tube, dry carefully, and then heat in a tube. The mercury will sublime away from the surface of the copper and condense on the upper part of the tube.

Mercurous Compounds, Hg′

Use mercurous nitrate, $Hg(NO_3),2H_2O$.

*4. (*a*) When a solution of a mercurous salt is treated with dilute hydrochloric acid (HCl) a white precipitate of calomel (HgCl) is formed.

(*b*) The precipitate is insoluble in water.

(*c*) The precipitate is turned black by ammonium hydrate. The black substance is mercurous ammonium chloride (NH_2Hg_2Cl).

Mercuric Compounds, Hg″

Use mercuric chloride, $HgCl_2$.

*5. (*a*) To a solution of the salt add dilute hydrochloric acid. No precipitate is formed (distinction from mercurous salts).

(*b*) Pass sulphuretted hydrogen (H_2S) through the solution. A black precipitate of mercuric sulphide (HgS) is formed. The precipitate may commence by being white and get gradually darker and eventually black.

The precipitate is insoluble in 50 per cent. nitric acid (distinction from lead, copper and bismuth). It may turn grey or white on boiling with nitric acid. When dried and treated as in test No. 1 (mercury) it gives the deposit of mercury on the upper part of the tube.

*6. Mercuric salts in solution give with potassium iodide (KI) a precipitate which is first yellow, but which immediately changes to a bright red colour. It is mercuric iodide (HgI_2).

SUMMARY

From a study of the above-mentioned reactions it will be seen that—

(1) Silver and mercurous salts are precipitated by dilute hydrochloric acid.

(2) Lead is partially precipitated by dilute hydrochloric acid.

(3) Mercuric salts are not precipitated by dilute hydrochloric acid.

EXPT. 179.—**Examine the given substances for the presence of lead, silver or mercury.**

If, in a solution of an unknown salt, a white precipitate is obtained on the addition of dilute hydrochloric acid, the precipitate may be the chloride of silver, mercury(ous) or lead.

(If the solution is very dilute, lead may not be precipitated at all.)

To a portion of the precipitate add ammonium hydrate.

The precipitate dissolves. Add dilute nitric acid to the solution. A white precipitate indicates the presence of SILVER.	The precipitate turns black. Apply test No. 1 for mercury to this black mass A mirror confirms the presence of a MERCUROUS compound.	If the precipitate is neither soluble nor blackens, boil some with water ; salt dissolves ; reprecipitates on cooling. LEAD is present ; confirm by lead tests given above.

Equations (Group I)

Silver

1. What probably happens may be roughly represented,

	$2AgNO_3$	+	Na_2CO_3	=	$2NaNO_3$	+	Ag_2CO_3
	Silver nitrate	with	Sodium carbonate	gives	Sodium nitrate	and	Silver carbonate

Ag_2CO_3	=	CO_2	+	Ag_2O
Silver carbonate	gives	Carbon dioxide	and	Silver oxide

2.	$2Ag_2O$	+	C	=	$4Ag$	+	CO_2
	Silver oxide	with	Carbon	gives	Metallic silver	and	Carbon dioxide

Also	$2AgNO_3$	=	$2AgNO_2$	+	O_2	etc.
	Silver nitrate	gives	Silver nitrite	and	Oxygen	

$AgNO_2$, on heating, splits up, leaving silver.

3. (*a*)	$AgNO_3$	+	HCl	=	AgCl	+	HNO_3
	Silver nitrate	and	Hydrochloric acid	give	Silver chloride (white)	and	Nitric acid

(*b*) and (*c*) The silver chloride is soluble in ammonium hydroxide, forming a complex compound which is decomposed by dilute nitric acid.

4. (*a*)	$2AgNO_3$	+	K_2CrO_4	=	Ag_2CrO_4	+	$2KNO_3$
	Silver nitrate	and	Potassium chromate	give	Silver chromate (red precipitate)	and	Potassium nitrate

(*b*)	Ag_2CrO_4	+	$2HCl$	=	$2AgCl$	+	H_2CrO_4
	Silver chromate	and	Hydrochloric acid	give	Silver chloride (white precipitate)	and	Chromic acid

Lead

3.	$Pb(NO_3)_2$	+	$2HCl$	=	$PbCl_2$	+	$2HNO_3$
	Lead nitrate	and	Hydrochloric acid	give	Lead chloride (white precipitate)	and	Nitric acid

4. $Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3$
Lead nitrate and Potassium chromate give Lead chromate (yellow precipitate) and Potassium nitrate

5. $Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$
Lead nitrate and Sulphuric acid give Lead sulphate and Nitric acid

6. $Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$
Lead nitrate and Sulphuretted hydrogen give Lead sulphide and Nitric acid

Mercury

3. $Hg(NO_3)_2 + Cu = Cu(NO_3)_2 + Hg$
Mercuric nitrate and Copper give Copper nitrate and Mercury

4. (*a*) $HgNO_3 + HCl = HgCl + HNO_3$
Mercurous nitrate and Hydrochloric acid give Mercurous chloride (calomel) and Nitric acid

5. $HgCl_2 + H_2S = HgS + 2HCl$
Mercuric chloride and Sulphuretted hydrogen give Mercuric sulphide (black precipitate) and Hydrochloric acid

6. $HgCl_2 + 2KI = HgI_2 + 2KCl$
Mercuric chloride and Potassium iodide give Mercuric iodide (red precipitate) and Potassium chloride

DEMONSTRATION 39

TESTS FOR METALS—GROUP II

Metals of the second group comprise mercuric, lead, copper, bismuth, cadmium, arsenic, antimony and tin.

Try to write equations representing the reactions marked with an asterisk (*). You will find the correct equations at the end of the demonstration (page 172).

The reactions of MERCURY and LEAD have already been studied.

EXPT. 180.—**Tests for Copper,** Cu.

Use copper sulphate, $CuSO_4,5H_2O$. Many copper salts are coloured blue or green, both in the solid state and in solution.

1. Mix a little of the powdered copper salt with sodium carbonate and a little potassium cyanide, and heat on charcoal under the blow-pipe flame. A residue of red flakes of metallic copper is found on the charcoal. The flakes do not run together owing to melting-point of copper being high.

2. Make a borax bead and put in it a minute quantity of a copper salt.

Heat strongly in the oxidising (outer) flame, use the mouth blow-pipe; the oxidising and reducing zones are easily defined.

In the oxidising (outer) flame the bead is green when hot, but turns blue on cooling. In the reducing flame the bead becomes reddish or opaque, due to the separation of metallic copper.

This red colour may be produced more easily if, before heating in the reducing flame, the bead is dipped in stannous chloride ($SnCl_2$).

3. Copper compounds colour the Bunsen flame green. If the substance be first moistened with concentrated hydrochloric acid

and then introduced into the Bunsen flame on a platinum wire the flame is coloured green, but after a time the colour changes to blue.

*4. To a solution of a copper salt add hydrochloric acid (HCl)—no precipitate.

Pass sulphuretted hydrogen (H_2S) through the solution—black precipitate of copper sulphide (CuS). Filter off the copper sulphide and dissolve it in 50 per cent. nitric acid (HNO_3).

Potassium cyanide prevents the precipitation of copper as copper sulphide.

*5. To a solution of a copper salt add ammonium hydrate (NH_4OH); a bluish-green precipitate of basic salt is first formed, but it dissolves in excess of ammonium hydrate, forming a beautiful blue solution. This test is very delicate.

*6. To a solution of a copper salt add a solution of potassium ferrocyanide [$K_4Fe(CN)_6$]. A chocolate brown precipitate of cupric ferrocyanide {$Cu_2[Fe(CN)_6]$} is thrown down (in very dilute solutions only a brown coloration may be produced).

Expt. 181.—**Tests for Cadmium,** Cd.

Use cadmium chloride, $CdCl_2,2H_2O$. Cadmium salts are generally white.

1. Mix some of the powdered cadmium salt with sodium carbonate and heat strongly on charcoal under the blow-pipe. A brown incrustation of cadmium oxide (CdO) is obtained.

2. Cadmium compounds give no colour in the borax bead nor to the Bunsen flame.

*3. To a solution of a cadmium salt add dilute hydrochloric acid—no precipitate. Pass sulphuretted hydrogen (H_2S) through the solution. Cadmium sulphide (CdS) is thrown down as a light yellow precipitate.

If the solution is too strongly acid the precipitate will not come down. Add water to the solution and pass sulphuretted hydrogen (H_2S). Cadmium sulphide is insoluble in ammonium sulphide [$(NH_4)_2S$], sodium hydrate (NaOH) and potassium cyanide (KCN). Cadmium sulphide (CdS) is soluble in dilute hydrochloric and nitric acids.

*4. To a solution of a cadmium salt add ammonium hydroxide

(NH_4OH). A white precipitate is formed and is soluble in excess of ammonium hydroxide.

EXPT. 182 —**Tests for Bismuth,** Bi.

Use Bismuth nitrate, $Bi(NO_3)_3,3H_2O$.

1. Mix some of the powdered salt with sodium carbonate and heat on charcoal under the blow-pipe. A metallic bead is formed which, when punched in the mortar, is found to be brittle. An incrustation of bismuth oxide (Bi_2O_3) is formed on the charcoal. It is orange-red when hot and light yellow when cold.

2. Bismuth compounds give no indication in the borax bead. When heated dry in a test-tube, the mass often looks orange-coloured when hot and pale yellow when cold. When heated in the Bunsen flame, a pale blue coloration is produced, but it is not distinctive.

*3. Through a solution of a bismuth salt in dilute hydrochloric acid pass sulphuretted hydrogen (H_2S) ; a dark brown or black precipitate of bismuth sulphide (Bi_2S_3) is then thrown down. It is easily soluble in 50 per cent. nitric acid (HNO_3).

*4. To a solution of a bismuth salt in dilute hydrochloric acid add excess of water. A basic salt ($BiOCl$) is thrown down. This precipitate is insoluble in tartaric acid (distinction from antimony).

*5. To the solution of a bismuth salt add a solution of ammonium hydrate (NH_4OH) ; a white precipitate is thrown down which is insoluble in excess of ammonium hydrate.

EXPT. 183.—**Test the given substances for the presence of mercury(ic), lead, bismuth, copper, or cadmium compounds.**

SUMMARY

From the foregoing tests for mercury(ic), lead, copper, cadmium, and bismuth it will be seen that—

(1) Lead is partially precipitated by dilute hydrochloric acid, but that mercur(ic), copper, cadmium, and bismuth are not precipitated.

(2) All these five metals are precipitated by sulphuretted hydrogen in the presence of dilute hydrochloric acid.

(3) Cadmium sulphide is yellow and insoluble in ammonium sulphide and caustic soda.

(4) The other sulphides are black or nearly black; of these, mercuric sulphide is the only one which is insoluble in 50 per cent. nitric acid.

These metals may be detected by means of the following table.

Acidify the solution of your salt with dilute hydrochloric acid—no precipitate (∴ Group I. absent). Through the solution pass sulphuretted hydrogen. A precipitate is formed; filter, wash

Precipitate is black. Warm with 50% nitric acid				Precipitate is yellow
Precipitate is insoluble; it may turn grey or white. Mix up with dry sodium carbonate and potassium nitrate. Heat in a bulb-tube A mirror indicates the presence of MERCURY(IC)	The precipitate dissolves. Evaporate the solution down, or, better, take the original solution.			Warm with ammonium sulphide or sodium hydrate Precipitate does not dissolve, CADMIUM is present.
	A Add dilute sulphuric acid; a white precipitate soluble in ammonium acetate indicates the presence of LEAD.	B. Add ammonium hydrate A white precipitate soluble in hydrochloric acid, but reprecipitated on large dilution with water, indicates the presence of BISMUTH	B Add ammonium hydrate, the solution turns a brilliant blue colour; COPPER is present.	

Equations (Group II.) (*a*).

Copper

4.	$CuSO_4$	$+$	H_2S	$=$	CuS	$+$	H_2SO_4
	Copper sulphate	with	Sulphuretted hydrogen	gives	Cupric sulphide (black precipitate)	and	Sulphuric acid
	CuS	$+$	$2HNO_3$	$=$	$Cu(NO_3)_2$	$+$	H_2S
	Copper sulphide	with	Nitric acid	gives	Copper nitrate	and	Sulphuretted hydrogen

The sulphuretted hydrogen will be partly oxidised by the nitric acid. Some sulphur may remain in the solution in suspension.

5.	$2CuSO_4$	$+$	$2NH_4 \cdot OH$	$=$	$CuSO_4,Cu(OH)_2$	$+$	$(NH_4)_2SO_4$
	Copper sulphate	and	Ammonium hydrate	give	Basic copper sulphate	and	Ammonium sulphate

$CuSO_4,Cu(OH)_2$	$+$	$6NH_4{\cdot}OH$	$+$	$(NH_4)_2SO_4$
Basic copper sulphate	with	excess of ammonium hydrate	and	Ammonium sulphate

$=$	$2(CuSO_4,4NH_3)$	$+$	$8H_2O.$
gives	(Blue solution)	and	Water

6.	$2CuSO_4$	$+$	$K_4Fe(CN)_6$	$=$	$Cu_2Fe(CN)_6$	$+$	K_2SO_4
	Copper sulphate	with	Potassium ferrocyanide	gives	Cupric ferrocyanide (brown precipitate)	and	Potassium sulphate

Cadmium

3.	$CdCl_2$	$+$	H_2S	$\rightleftharpoons$	CdS	$+$	$2HCl$
	Cadmium chloride	with	Sulphuretted hydrogen	gives	Cadmium sulphide (yellow precipitate)	and	Hydrochloric acid

This reaction is reversible.

4.	$CdCl_2$	$+$	$2NH_4{\cdot}OH$	$=$	$Cd(OH)_2$	$+$	$2NH_4Cl$
	Cadmium chloride	and	Ammonium hydrate	give	Cadmium hydrate (white precipitate soluble in excess of $NH_4{\cdot}OH$)	and	Ammonium chloride

Bismuth

3.	$2Bi(NO_3)_3$	$+$	$3H_2S$	$\rightleftharpoons$	Bi_2S_3	$+$	$6HNO_3$
	Bismuth nitrate	and	Sulphuretted hydrogen	give	Bismuth sulphide (brownish-black precipitate)	and	Nitric acid

This action is reversible.

4.	$BiCl_3$	$+$	H_2O	$=$	$BiOCl$	$+$	$2HCl$
	Bismuth chloride	and	Water (large volume)	give	Bismuth oxychloride (white precipitate)	and	Hydrochloric acid

5.	$Bi(NO_3)_3$	$+$	$3NH_4{\cdot}OH$	$=$	$Bi(OH)_3$	$+$	$3NH_4{\cdot}NO_3$
	Bismuth nitrate	with	Ammonium hydrate	gives	Bismuth hydroxide	and	Ammonium nitrate

DEMONSTRATION 40

TESTS FOR METALS—GROUP II. (*b*)—(*continued*)

Try to write equations representing the reactions marked with an asterisk (*). You will find the correct equations at the end of the demonstration (page 178).

EXPT. 184.—**Tests for Arsenic,** As.

For dry tests use arsenious oxide, As_2O_3.

For wet tests dissolve arsenious oxide in dilute hydrochloric acid.

1. When arsenic compounds are heated on charcoal under the blow-pipe flame a white fume is produced which smells strongly of garlic. This is characteristic of arsenic.

2. When mixed with some sodium carbonate and charcoal and heated in a bulb-tube, compounds of arsenic are reduced and a black, shining sublimate will form on the upper part of the tube.

The black sublimate is arsenic. It is soluble in sodium hypochlorite. (See below, "Marsh's Test.")

3. Arsenic compounds give a pale blue coloration to the Bunsen flame. A white, garlic-smelling vapour is also evolved.

4. Compounds of arsenic give no coloration to the borax bead.

*5. Through the solution of an arsenic salt pass sulphuretted hydrogen. A yellow precipitate of arsenious sulphide (As_2S_3) is thrown down. It is insoluble in concentrated or dilute hydrochloric acid; soluble in sodium hydrate or ammonium sulphide.

NOTE ON AMMONIUM SULPHIDE

When this reagent is mentioned, "yellow" ammonium sulphide must be used. It is not pure ammonium sulphide, as it contains the ammonium salts of thionic acids, and gives a precipitate of sulphur when treated with an acid. It is prepared by passing sulphuretted hydrogen through a solution of ammonia in which free sulphur is suspended. The reagent should give no precipitate with calcium or magnesium salts.

EXPT. 185.—**Tests for Antimony,** Sb.

Use antimony trichloride, $SbCl_3$.

To obtain a solution hydrochloric acid must be present.

1. When compounds of antimony are mixed with sodium carbonate, and heated on charcoal under the blow-pipe, brittle beads of antimony are formed. White fumes of antimonious oxide (Sb_2O_3) are given off (a little potassium cyanide assists the reduction).

2. Antimony compounds give no distinctive colour to the Bunsen flame or the borax bead.

*3. Through a solution of an antimony salt acidified with hydrochloric acid pass sulphuretted hydrogen. An orange-red precipitate of antimony sulphide (Sb_2S_3) is thrown down. The sulphide is soluble in strong hydrochloric acid, and, if the solution is too strongly acid, the sulphide may not be precipitated at all. It is also soluble in ammonium sulphide and sodium hydrate. (See also Expt. 95, page 99.)

*4. To a solution of an antimony salt add a very large bulk of water. An oxy-salt is precipitated. The precipitate is soluble in tartaric acid (distinction from bismuth).

5. To a solution of an antimony salt in hydrochloric acid (nitric acid must be absent) add a piece of platinum foil. Now insert some zinc so that it is in contact with the platinum. A black stain of metallic antimony on the platinum indicates the presence of antimony.

DEMONSTRATION (Marsh's test)

This is a very delicate test for arsenic and antimony.

An apparatus for generation of hydrogen is fitted up. Pure zinc is put in it and one or two drops of copper sulphate solution. Dilute (pure) sulphuric acid is poured down the funnel and the action allowed to proceed until all the air is expelled from the

Woulfe's bottle (test). A glass jet is fixed on to the delivery tube. As soon as the hydrogen burns quietly blow out the flame. Pour into the thistle funnel a little of a solution containing arsenic. Test the hydrogen to see if it is pure before again igniting the jet. Allow the burning hydrogen to play on to a cool white surface (evaporating basin). A black deposit indicates the presence of arsenic or antimony.

If it is *antimony* it is *insoluble* in sodium hypochlorite solution (NaOCl).

If it is *arsenic* it is *soluble* in sodium hypochlorite (NaOCl). Prepare your sodium hypochlorite when required by adding chlorine water to cold caustic soda solution.

$$2NaOH + Cl_2 = NaCl + NaClO.$$

(The student can recollect that arsenic is soluble by remembering that "arsenic" has an "s" in it and antimony has no "s.")

EXPT 186.—**Tests for Tin,** Sn.

There are two classes of tin compounds: Those in which tin behaves as a divalent element, called STANNOUS compounds, and those in which tin behaves as a tetravalent element, called STANNIC compounds.

1. Mix any compound of tin with sodium carbonate and heat the mixture on charcoal under the blow-pipe flame. A little potassium cyanide assists the reduction. Malleable beads of tin are obtained.

2. Tin compounds give no characteristic colour with borax bead nor in the Bunsen flame.

*3. To a solution of a tin salt acidulated with dilute hydrochloric acid add a piece of platinum foil and then zinc in contact with the platinum foil.

The platinum foil remains bright, but a spongy deposit of tin forms over the surface of the zinc. If this spongy deposit be now dissolved in hydrochloric acid the solution of stannous chloride ($SnCl_2$) so produced will reduce mercuric chloride ($HgCl_2$) in solution first to calomel (HgCl) and finally to mercury (Hg), a greyish-black coloured mass.

*4. If sulphuretted hydrogen is passed through a solution of a stannous salt, acidulated with hydrochloric acid, a chocolate-brown coloured precipitate of stannous sulphide (SnS) is produced. It is soluble in ammonium sulphide and strong hydrochloric acid.

*5. If sulphuretted hydrogen (H_2S) is passed through a solution of a stannic salt, acidulated with hydrochloric acid, a yellow precipitate of stannic sulphide (SnS_2) is thrown down. It is soluble in ammonium sulphide.

Expt. 187.—**Examine the given substances for the presence of compounds of arsenic, antimony, or tin.**

Summary

From the foregoing tests for arsenic, antimony and tin it will be seen that—

(1) Arsenic, antimony, and tin are precipitated as sulphides by sulphuretted hydrogen in the presence of hydrochloric acid.

(2) Arsenic sulphide is not soluble in concentrated hydrochloric acid. The sulphides of antimony and tin are soluble in concentrated hydrochloric acid.

(3) If, to a solution which may contain antimony or tin, some platinum foil and zinc be added, a black deposit on platinum indicates the presence of *antimony*. A spongy residue soluble in strong hydrochloric acid may be *tin*. (*Vide* Expt. 186, No. 2.)

These facts may be tabulated thus :-

Through a solution of the salt, acidulated with hydrochloric acid, pass sulphuretted hydrogen.

A coloured precipitate is produced.

The precipitate is soluble in ammonium sulphide.

To the solution add strong hydrochloric acid and boil.

<table>
<tr>
<td rowspan="2">Yellow precipitate insoluble in boiling hydrochloric acid—
ARSENIC present (confirm)</td>
<td colspan="2">No precipitate, or the precipitate first formed redissolves. To the solution add platinum foil and metallic zinc</td>
</tr>
<tr>
<td>Black stain on the platinum indicates the presence of
ANTIMONY.</td>
<td>No black stain on platinum. Completely dissolve residue in hydrochloric acid. To the solution add mercuric chloride solution. A white precipitate, turning grey on warming, indicates the presence of
TIN.</td>
</tr>
</table>

Equations—Group II. (*b*).

Arsenic

5.	$2AsCl_3$	$+$	$3H_2S$	$=$	As_2S_3	$+$	$6HCl$
	Arsenic trichloride	and	Sulphuretted hydrogen	give	Arsenic trisulphide (yellow precipitate)	and	Hydrochloric acid

As_2S_3	$+$	$3(NH_4)_2S$	$=$	$2(NH_4)_3AsS_3$
Arsenic trisulphide	and	Ammonium sulphide (yellow)	give	Ammonium thioarsenite

Antimony

3.	$2SbCl_3$	$+$	$3H_2S$	$\rightleftarrows$	Sb_2S_3	$+$	$6HCl$
	Antimony trichloride	with	Sulphuretted hydrogen	gives	Antimony trisulphide (orange-coloured precipitate)	and	Hydrochloric acid

This reaction is reversible. (See Expt. 95, page 99.)

Sb_2S_3	$+$	$3(NH_4)_2S$	$=$	$2(NH_4)_3SbS_3$
Antimony trisulphide	and	Ammonium sulphide (yellow)	give	Ammonium thioantimonite

4.	$SbCl_3$	$+$	H_2O	$=$	$SbOCl$	$+$	$2HCl$
	Antimony trichloride	with	large excess of water	gives	Antimony oxychloride	and	Hydrochloric acid

Tin

3.	$SnCl_2$	$+$	Zn	$=$	$ZnCl_2$	$+$	Sn
	Stannous chloride	and	Zinc	give	Zinc chloride	and	Metallic (spongy) tin
	$SnCl_4$	$+$	$2Zn$	$=$	$2ZnCl_2$	$+$	Sn
	Stannic chloride	and	Zinc	give	Zinc chloride	and	Metallic (spongy) tin
	Sn	$+$	$2HCl$	$=$	$SnCl_2$	$+$	H_2
	Tin	with	Hydrochloric acid	gives	Stannous chloride	and	Hydrogen

$SnCl_2$	$+$	$2HgCl_2$	$=$	$SnCl_4$	$+$	$2HgCl$
Stannous chloride	and	Mercuric chloride	give	Stannic chloride	and	Mercurous chloride calomel (white precipitate)

$SnCl_2$	$+$	$2HgCl$	$=$	$SnCl_4$	$+$	Hg
Stannous chloride	and	Calomel	give	Stannic chloride	and	Metallic mercury (grey precipitate)

4.

$SnCl_2$	$+$	H_2S	$\rightleftarrows$	SnS	$+$	$2HCl$
Stannous chloride	with	Sulphuretted hydrogen	gives	Stannous sulphide (soluble in yellow ammonium sulphide)	and	Hydrochloric acid

This reaction is reversible.

5.

$SnCl_4$	$+$	$2H_2S$	$\leftrightarrows$	SnS_2	$+$	$4HCl$
Stannic chloride	and	Sulphuretted hydrogen	give	Stannic sulphide	and	Hydrochloric acid

DEMONSTRATION 41

TESTS FOR METALS—GROUP III

Try to write equations representing the reactions marked with an asterisk (*). You will find the correct equations at the end of the demonstration.

EXPT. 188.—**Tests for Iron,** Fe.

There are two classes of iron compounds—

(1) Those in which iron behaves as a divalent metal, called FERROUS salts, and

(2) Those in which iron behaves as a trivalent metal, called FERRIC salts.

Reactions which are obtained with both "ferrous" and "ferric" compounds.

Use any compound of iron.

1. Compounds of iron give no very definite indication when heated under the blow-pipe on charcoal. A magnetic residue may be obtained. Iron compounds give no characteristic colour to the Bunsen flame.

2. Make a borax bead. Put in it a minute quantity of an iron compound.

Heated in the outer (oxidising) flame, a bead is produced which is *dark red* when hot, but turns *yellow* on cooling.

Heated in the inner (reducing) flame, a *bottle-green* coloured bead is obtained.

*3. To a solution of any iron salt add a little nitric acid (HNO_3); boil, cool. (1) Add ammonium hydroxide, a reddish-brown coloured precipitate of ferric hydroxide [$Fe_2(OH)_6$] is obtained.

(2) Dissolve the precipitate in dilute hydrochloric acid (HCl).

To the solution add potassium ferrocyanide solution [$K_4Fe(CN)_6$]. A blue coloration or precipitate indicates the presence of iron.

4. To a solution of a compound of iron add dilute hydrochloric acid—no precipitate. Pass sulphuretted hydrogen through the solution—no precipitate.

Ferrous Compounds

Use ferrous sulphate, $FeSO_4,7H_2O$.

*5. (*a*) To a solution of the ferrous salt add a solution of potassium ferrocyanide [$K_1Fe(CN)_6$]—a *bluish-white* precipitate of ferrous ferrocyanide, $K_2Fe[Fe(CN)_6]$, is produced.

(*b*) This bluish-white precipitate changes to a bright blue colour (Prussian blue) on standing exposed to the air or on treatment with an oxidising agent.

*6. To the faintly acid solution of a ferrous salt add freshly prepared solution of potassium ferricyanide [$K_3Fe(CN)_6$]—a dark blue precipitate of ferrous ferricyanide {$Fe_3[Fe(CN)_6]_2$} (Turnbull's blue) is thrown down.

*7. Ammonium sulphide gives a black precipitate of ferrous sulphide (FeS) soluble in dilute mineral acids.

Ferric Compounds

Use ferric chloride, $FeCl_3,6H_2O$.

*8. To a solution of the salt add potassium ferrocyanide solution [$K_4Fe(CN)_6$]—a fine blue precipitate of ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, (Prussian blue), is obtained. The precipitate is insoluble in hydrochloric acid.

9. To a solution of the salt add potassium ferricyanide [$K_3Fe(CN)_6$] solution—a brown or reddish-brown coloration is obtained.

*10. (*a*) To a solution of the salt add potassium ($KCNS$) or ammonium sulphocyanide [$(NH_4)CNS$] solution—a blood-red coloration of ferric sulphocyanide [$Fe(CNS)_3$] is produced.

(*b*) This coloration is destroyed by mercuric chloride ($HgCl_2$) solution.

This is a delicate test for ferric salts.

Remember that if you wish to discover whether the given substance is a "ferrous" or "ferric" compound, the tests must be performed on the original substance itself.

EXPT. 189.—**Chromium,** Cr.

Use green chromium chloride, $CrCl_3,6H_2O$.

1. Compounds of chromium give no very definite indication when heated under the blow-pipe on charcoal, nor do they give any characteristic colour in the Bunsen flame.

2. Make a borax bead. Put on it a minute quantity of a chromium compound. Heated in either the outer (oxidising) or the inner (reducing) flame an *emerald green* bead is produced.

*3. Take any chromium compound and intimately mix it with some sodium carbonate (Na_2CO_3) anhydrous, some solid caustic soda and a little potassium nitrate (KNO_3). Ignite the mixture strongly on a piece of porcelain (a piece of broken evaporating basin does admirably) and a yellow mass is obtained. Cool the mass and dissolve it in water. Filter. To the filtrate add sufficient dilute hydrochloric acid to neutralise the sodium carbonate and sodium hydrate present. Now add to the solution sulphurous acid (SO_2Aq). The solution turns *green.*

*4. Boil a solution of a chromium salt with ammonium chloride (NH_4Cl). Cool the solution. Add to it ammonium hydrate ($NH_4 \cdot OH$). A dirty green precipitate of chromium hydroxide [$Cr(OH)_3$] is produced. Filter this off and apply test No. 3 (above) to it.

EXPT. 190.—**Aluminium,** Al.

Use alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, or aluminium chloride, $AlCl_3,6H_2O$.

1. Aluminium compounds, when heated on charcoal before the blow-pipe flame, give a white mass which becomes brightly incandescent when strongly heated. Cool. Add two drops of cobalt nitrate or chloride to the white mass and heat again in the inner blow-pipe flame. A blue-coloured mass is obtained (distinction from zinc).

2. Aluminium compounds give no indication when heated in the borax bead and no definite coloration to the Bunsen flame.

3. Boil a solution of an aluminium salt with ammonium chloride (NH_4Cl) ; cool.

* (*a*) Add ammonium hydroxide ($NH_4 \cdot OH$). A white, gelatinous precipitate of aluminium hydroxide [$Al(OH)_3$] is produced.

* (*b*) This precipitate, $Al(OH)_3$, is soluble in sodium hydroxide (cf. Zinc).

(*c*) On boiling the solution produced in (*b*) with ammonium chloride (NH_4Cl) the aluminium hydroxide is re-precipitated (distinction from magnesium).

Expt. 191.—**Examine the given substances for the presence of compounds of iron, chromium, or aluminium.**

Summary

From the foregoing tests we see that iron, aluminium, and chromium are all precipitated by ammonium hydrate. The solution has first to be boiled with ammonium chloride in order to prevent the precipitation of certain other metals, *e.g.*, manganese, magnesium, etc. Before adding the ammonium chloride, always boil the solution with one or two drops of nitric acid, because, if iron is present, it is necessary to oxidise it to the "ferric" state in order to ensure its complete precipitation by ammonium hydrate.

In order to identify iron, aluminium, or chromium in a solution, boil with a few drops of concentrated nitric acid; add ammonium chloride, boil and then cool.

Add ammonium hydrate slowly until the solution just smells of ammonia after stirring; a precipitate is formed.

The precipitate is white— ALUMINIUM is present. Confirm by the tests on page 182.	The precipitate is reddish-brown— IRON is present. Dissolve a little of the precipitate in dilute hydrochloric acid. Add a solution of potassium ferrocyanide. A blue precipitate or coloration confirms IRON.	The precipitate is dirty green— CHROMIUM is present. Confirm by test No 4 Use the precipitate for the test. (A dirty green precipitate may be due to ferrous hydroxide. This can only happen if you have neglected the preliminary oxidation with nitric acid.)

Note to Demonstrators

For testing for chromium in solution, prepare a solution by acidifying a solution of potassium chromate and boiling it with a solution of sulphur dioxide in water till the chromate is reduced and the solution smells no longer of sulphur dioxide.

Equations (Group III)

Iron

3. (*a*)	$2FeSO_4$	$+$	O	$+$	H_2SO_4	$=$	$Fe_2(SO_4)_3$	$+$	H_2O
	Ferrous sulphate	with an	Oxidising agent	and	Acid	gives	Ferric sulphate	and	Water

(*b*).	$Fe_2(SO_4)_3$	$+$	$6(NH_4 \cdot OH)$	$+$	$2Fe(OH)_3$	$+$	$3(NH_4)_2SO_4$
	Ferric sulphate	with	Ammonium hydrate	gives	Ferric hydroxide (reddish-brown precipitate)	and	Ammonium sulphate

5. (*a*)	$FeSO_4$	$+$	$K_4Fe(CN)_6$	$=$	$K_2Fe''[Fe(CN)_6]$	$+$	K_2SO_4
	Ferrous sulphate	and	Potassium ferrocyanide	give	Potassium ferrous ferrocyanide	and	Potassium sulphate

(*b*)	$4K_2Fe''[Fe(CN)_6]$	$+$	O_2	$+$	$2H_2SO_4$
	Potassium ferrous ferrocyanide (bluish precipitate)		exposed to air		

$=$	$2K_2SO_4$	$+$	$2H_2O$	$+$	$K_4Fe(CN)_6$	$+$	$Fe_7(CN)_{18}$
gives	Potassium sulphate	and	Water	and	Potassium ferrocyanide	and	Prussian blue

6.	$3FeSO_4$	$+$	$2K_3Fe(CN)_6$	$=$	$Fe_3[Fe(CN)_6]_2$	$+$	$3K_2SO_4$
	Ferrous sulphate	and	Potassium ferricyanide	give	Ferrous ferricyanide (Turnbull's blue)	and	Potassium sulphate

7.	$FeSO_4$	$+$	$(NH_4)_2S$	$=$	FeS	$+$	$(NH_4)_2SO_4$
	Ferrous sulphate	with	Ammonium sulphide	gives	Ferrous sulphide	and	Ammonium sulphate

8.	$3K_4Fe(CN)_6$	$+$	$4FeCl_3$	$=$	$12KCl$	$+$	$Fe_4[Fe(CN)_6]_3$
	Potassium ferrocyanide	and	Ferric chloride	give	Potassium chloride	and	Ferric ferrocyanide

10. $FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$

Ferric chloride and Potassium sulphocyanide give Ferric sulphocyanide and Potassium chloride

11. $2FeCl_3 + 3(NH_4)_2S = 2FeS + 6NH_4Cl + S$

Ferric chloride and Ammonium sulphide give Ferrous sulphide and Ammonium chloride and Sulphur

Chromium

3. (*a*) $2Cr(OH)_3 + 2Na_2CO_3 + 3O$

Chromium hydrate with Sodium carbonate and Oxidising agent

$= 2Na_2CrO_4 + 2CO_2 + 3H_2O$

gives Sodium chromate and Carbon dioxide and Water

(*b*) $2Na_2CrO_4 + 2HCl = 2NaCl + Na_2Cr_2O_7 + H_2O$

Sodium chromate with Dilute hydrochloric acid gives Sodium chloride Sodium bichromate Water

(*c*) $Na_2Cr_2O_7 + H_2SO_4 + 3SO_2$

Sodium bichromate with Sulphuric acid and Sulphur dioxide

$= Cr_2(SO_4)_3 + Na_2SO_4 + H_2O$

gives Chromic sulphate and Sodium sulphate Water

4. $CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl$

Chromic chloride and Ammonium hydrate give Chromium hydroxide (dirty green precipitate) and Ammonium chloride

Aluminium

3. (*a*) $AlCl_3 + 3NH_4{\cdot}OH = Al(OH)_3 + 3NH_4Cl$

Aluminium chloride and Ammonium hydrate give Aluminium hydroxide and Ammonium chloride

(*b*) $Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$

Aluminium hydroxide with Sodium hydrate gives Sodium aluminate in solution and Water

(*c*) $NaAlO_2 + NH_4Cl + H_2O$

Sodium aluminate boiled with Ammonium chloride and Water

$= Al(OH)_3 + NaCl + NH_3$

gives Aluminium hydroxide and Sodium chloride and Ammonia

DEMONSTRATION 42

TESTS FOR METALS—GROUP IV

Try to write equations representing the reactions marked with an asterisk (*). You will find the correct equations at the end of the demonstration (page 190).

EXPT. 192.—**Cobalt, Co.**

Use cobalt nitrate, $Co(NO_3)_2,6H_2O$, or cobalt chloride, $CoCl_2,6H_2O$.

Most cobalt salts give a pink solution in water.

1. Cobalt compounds give no characteristic action when heated on charcoal under the blow-pipe, or any definite coloration to the Bunsen flame.

2. Make a borax bead, put in it a minute quantity of the cobalt salt. Heat in the outer (oxidising) flame, or in the inner (reducing) flame. The bead is a fine sapphire-blue colour.

3. Boil a solution of a cobalt salt with ammonium chloride (NH_4Cl) ; cool.

(*a*) Add ammonium hydrate—no precipitate.

*(*b*) Pass sulphuretted hydrogen (H_2S) through the ammoniacal solution—a black precipitate of cobalt sulphide (CoS) is thrown down.

(*c*) The precipitate is insoluble in excess of ammonium sulphide [$(NH_4)_2S$] and in dilute hydrochloric acid.

(*d*) The precipitate is soluble in dilute hydrochloric acid (HCl) to which a crystal of potassium chlorate ($KClO_3$) has been added. This is due to the action of "nascent" chlorine. (See Expt. 44B, page 47.)

Optional—

*4. To the solution of the cobalt salt add potassium cyanide (KCN) solution drop by drop. A brownish-coloured precipitate of cobalt cyanide [$Co(CN)_2$] is produced which dissolves in potassium cyanide. (Avoid large excess of potassium cyanide.) Potassium cobaltocyanide [$K_4Co(CN)_6$] is produced. Add sodium hydrate ($NaOH$) and bromine water ($BrAq$). No precipitate is produced, but the cobaltocyanide [$K_4Co(CN)_6$] is oxidised to cobalticyanide [$K_3Co(CN)_6$].

EXPT. 193.—**Nickel,** Ni.

Use nickel sulphate, $NiSO_4,7H_2O$.

Most nickel salts give a green solution in water.

1. Nickel compounds give no characteristic action when heated on charcoal under the blow-pipe, nor any definite coloration to the Bunsen flame.

2. Make a borax bead, put in it a minute quantity of the nickel salt.

Heat in the outer (oxidising) flame; the bead is coloured violet-brown when hot, and yellowish-red when cold. (A trace of potassium nitrate (KNO_3) assists this test.)

Heat in the inner (reducing) flame; the bead is coloured grey. The grey colour is due to particles of finely-divided nickel.

3. Boil a solution of a nickel salt with ammonium chloride (NH_4Cl).

(*a*) Cool, add ammonium hydrate ($NH_4 \cdot OH$)—no precipitate.

*(*b*) Pass sulphuretted hydrogen (H_2S) through the ammoniacal solution—a black precipitate of nickel sulphide (NiS) is thrown down.

(*c*) The precipitate (NiS) is difficultly soluble in hydrochloric acid, but dissolves readily on adding a small crystal of potassium chlorate ($KClO_3$). (The solvent action is due to the action of nascent chlorine.)

NOTE.—If ammonium sulphide is used to precipitate the nickel sulphide instead of passing sulphuretted hydrogen through the ammoniacal solution a black-coloured solution may be obtained. This is due to the solubility of nickel sulphide in ammonium sulphide. The nickel sulphide may be precipitated from this dark solution by the addition of acetic acid.

Optional—

*4. To the solution of the nickel salt add potassium cyanide.

(KCN) solution drop by drop. A yellowish-green precipitate of nickel cyanide [$Ni(CN)_2$] is produced, which dissolves in potassium cyanide, forming a brown solution containing a double salt [$K_2Ni(CN)_4$.]. (Avoid large excess of potassium cyanide.) To the solution add sodium hydrate and bromine water (BrAq) or strong sodium hypochlorite (NaOCl) solution. A black precipitate of nickelic hydroxide [$Ni(OH)_3$] is thrown down.

Expt. 194.—**Manganese,** Mn.

Use manganese sulphate, $MnSO_4,4H_2O$.

Salts of manganese have a pale pink colour and give a colourless or pale pink solution in water. Many manganates are green, many permanganates are violet or pink.

1. Manganese compounds give no characteristic reaction when heated on charcoal under the blow-pipe, nor any definite coloration to the Bunsen flame.

2. Make a borax bead and put in it a minute quantity of the manganese salt.

Heated in the outer (oxidising) flame the bead is coloured amethyst.

Heated in the inner (reducing) flame the bead becomes practically colourless.

*3. (*a*) Mix some of the manganese compound with fusion mixture (a mixture of sodium and potassium carbonates) and a little potassium nitrate (KNO_3). Heat strongly on platinum or on a piece of porcelain (a piece of broken evaporating basin serves the purpose admirably). Hold the porcelain in a pair of iron tongs and use the foot blow-pipe. A green colour should be produced. If there is any difficulty in getting this green colour allow the mass to cool and then add some solid sodium hydrate and heat again. The green colour is due to the presence of alkali manganate (Na_2MnO_4) which dissolves in water, giving a green solution. (*b*) This green solution is turned pink due to the formation of sodium permanganate ($NaMnO_4$) by the action of dilute sulphuric acid. This solution may turn pink without the addition of sulphuric acid if much water is added.

*4. Boil a solution of a manganese salt with ammonium chloride (NH_4Cl); cool.

(*a*) Add ammonium hydrate ($NH_4{\cdot}OH$). No precipitate should be formed. Keep out of air contact as much as possible.

*(*b*) Pass sulphuretted hydrogen (H_2S) through the ammoniacal solution—a buff- or pinkish-coloured precipitate of manganese sulphide (MnS) is produced. (The colour of precipitate may vary from dirty yellowish-white to a distinct pink colour.)

*(*c*) This precipitate is easily soluble in dilute mineral acids.

*(*d*) This precipitate is soluble in dilute acetic acid ($CH_3{\cdot}COOH$) (distinction from zinc).

EXPT. 195.—**Zinc,** Zn.

Use zinc sulphate, $ZnSO_4,7H_2O$.

1. Zinc compounds give no characteristic colour to the Bunsen flame nor to the borax bead.

2. When the powdered zinc salt is heated on charcoal under the blow-pipe a white mass of zinc oxide (ZnO) is obtained. This glows when hot and is of a yellow colour. On cooling it turns white. Moisten this white mass with two drops of cobalt chloride or nitrate and heat again under the blow-pipe. A bright green mass is obtained. (*Cf.* Aluminium, page 182.)

3. Boil the solution of a zinc salt with ammonium chloride (NH_4Cl) and cool.

(*a*) Add ammonium hydrate ($NH_4{\cdot}OH$). No precipitate.

*(*b*) Pass sulphuretted hydrogen (H_2S) through the ammoniacal solution. A white precipitate of zinc sulphide (ZnS) is thrown down.

*(*c*) The white precipitate is soluble in dilute mineral acids.

*(*d*) The white precipitate (ZnS) is insoluble in acetic acid ($CH_3{\cdot}COOH$) (distinction from manganese).

*4. (*a*) To a solution of a zinc salt add a solution of sodium hydrate ($NaOH$). A white precipitate of zinc hydroxide [$Zn(OH)_2$] is produced.

*(*b*) The zinc hydroxide is soluble in excess of sodium hydroxide.

*(*c*) Pass sulphuretted hydrogen (H_2S) through the solution. A white precipitate of zinc sulphide (ZnS) is thrown down.

EXPT. 196.—**Examine the given substances for the presence of cobalt, nickel, manganese, or zinc.**

SUMMARY

From the foregoing tests for cobalt nickel, manganese, and zinc it will be seen that—

(1) None of these metals is precipitated by ammonium chloride or ammonium hydrate in presence of ammonium chloride.

(2) All these metals are precipitated by sulphuretted hydrogen in the presence of ammonium hydrate.

(3) Two of the sulphides are black, viz., cobalt sulphide and nickel sulphide.

(4) Two of the sulphides are not black.

(5) If the sulphide is not black and is soluble in acetic acid, it is manganese sulphide; if it is white and insoluble in acetic acid, it is zinc sulphide.

(6) Both the light-coloured sulphides are soluble in dilute hydrochloric acid.

(7) Zinc hydroxide is soluble in excess of sodium hydrate.

Table for the identification of the metals of GROUP IV.

The precipitate is black.		The precipitate is not black.	
Examine by bead tests.		Dissolve the precipitate in dilute hydrochloric acid. Add sodium hydrate—a precipitate is formed.	
Blue bead in both oxidising and reducing flames indicates the presence of COBALT.	Violet-red bead in oxidising flame, grey bead in reducing flame, indicates the presence of NICKEL.	(1) It is soluble in excess of sodium hydrate. Pass sulphuretted hydrogen through the solution. White precipitate indicates the presence of ZINC.	(2) It is insoluble in excess of sodium hydrate. Filter off precipitate. Mix with fusion mixture and caustic soda (solid) and heat on porcelain. Green mass turning pink on solution in dilute sulphuric acid indicates the presence of MANGANESE.

Equations (Group IV)

Cobalt

3. (*b*)	$Co(NO_3)_2$	$+$	$(NH_4)_2S$	$=$	CoS	$+$	$2NH_4 \cdot NO_3$
	Cobalt nitrate	with	Ammonium sulphide	gives	Cobalt sulphide (black precipitate)	and	Ammonium nitrate

4. (*a*)	$Co(NO_3)_2$	+	$2KCN$	=	$Co(CN)_2$	+	$2KNO_3$
	Cobalt nitrate	with	Potassium cyanide	gives	Cobalt cyanide (yellowish-brown precipitate)	and	Potassium nitrate

(*b*)	$Co(CN)_2$	+	$4KCN$	=	$K_4Co(CN)_6$
	Cobalt cyanide	with	excess of Potassium cyanide	gives	Potassium cobaltocyanide (in solution)

(*c*)	$2K_4Co(CN)_6$	+	Br_2	=	$2K_3Co(CN)_6$	+	$2KBr$
	Potassium cobaltocyanide	with	Bromine	gives	Potassium cobalticyanide	and	Potassium bromide

Nickel

3. (*b*)	$NiSO_4$	+	$(NH_4)_2S$	=	NiS	+	$(NH_4)_2SO_4$
	Nickel sulphate	with	Ammonium sulphide	gives	Nickel sulphide (black precipitate)	and	Ammonium sulphate

4. (*a*)	$NiSO_4$	+	$2KCN$	=	$Ni(CN)_2$	+	K_2SO_4
	Nickel sulphate	with	Potassium cyanide	gives	Nickelous cyanide (yellowish-green precipitate)	and	Potassium sulphate

(*b*)	$Ni(CN)_2$	+	$2KCN$	=	$K_2Ni(CN)_4$
	Nickelous cyanide	with	excess of Potassium cyanide	gives	Potassium nickel cyanide (in solution)

(*c*)	$2K_2Ni(CN)_4$	+	$NaBrO$	+	$5H_2O$
	Potassium nickel cyanide	and	Sodium hypobromite (bromine and sodium hydrate)	and	Water

=	$Ni_2(OH)_6$	+	$NaBr$	+	$4HCN$	+	$4KCN$
give	Nickelic hydroxide (black precipitate)	and	Sodium bromide	and	Prussic acid	and	Potassium cyanide

NOTE—

$2NaOH$	+	Br_2	=	$NaBr$	+	$NaBrO$	+	H_2O
Sodium hydrate	and	Bromine	give	Sodium bromide	and	Sodium hypobromite	and	Water

The prussic acid formed would react with the excess of NaOH and give NaCN.

Manganese

3. (*a*)	$MnSO_4$	+	$2Na_2CO_3$	+	O_2
	Manganese sulphate	with	Fusion mixture	and	Air (oxidising agent)
=	Na_2MnO_4	+	Na_2SO_4	+	$2CO_2$
give	Sodium manganate (green mass)	and	Sodium sulphate	and	Carbon dioxide

(*b*)	$3Na_2MnO_4$	+	$3H_2O$
	Sodium manganate (green solution)	with	excess of Water

=	$2NaMnO_4$	+	$MnO_2(H_2O)$	+	$4NaOH$
gives	Sodium permanganate (pink solution)	and	Hydrated manganese dioxide	and	Sodium hydrate

4. (*b*)	$MnSO_4$	+	$(NH_4)_2S$	=	MnS	+	$(NH_4)_2SO_4$
	Manganese sulphate	with	Ammonium sulphide	gives	Manganese sulphide (light-coloured precipitate)	and	Ammonium sulphate

(*c*) and (*d*) MnS + dilute mineral acid (or acetic acid) gives sulphuretted hydrogen and the manganese salt of the acid.

Zinc

3. (*b*)	$ZnSO_4$	+	$(NH_4)_2S$	=	ZnS	+	$(NH_4)_2SO_4$
	Zinc sulphate	with	Ammonium sulphide	gives	Zinc sulphide (white precipitate)	and	Ammonium sulphate

(*c*) ZnS + dilute mineral acid gives sulphuretted hydrogen and the zinc salt of the acid.

4. (*a*)	$Zn(SO_4)$	+	$2Na(OH)$	=	$Zn(OH)_2$	+	Na_2SO_4
	Zinc sulphate	with	Sodium hydrate	gives	Zinc hydrate	and	Sodium sulphate
(*b*,	$Zn(OH)_2$	+	$2Na(OH)$	=	Na_2ZnO_2	+	H_2O
	Zinc hydrate	with	Excess of sodium hydrate	gives	Sodium zincate	and	Water
(*c*)	Na_2ZnO_2	+	H_2S	=	ZnS	+	$2NaOH$
	Sodium zincate	and	Sulphuretted hydrogen	gives	Zinc sulphide (white precipitate)	and	Sodium hydrate

DEMONSTRATION 43

TESTS FOR METALS—GROUP V

Try to write equations representing the reactions marked with an asterisk (*). You will find the correct equations at the end of the demonstration (page 197).

EXPT. 197.—**Barium,** Ba.

Use barium chloride, $BaCl_2,2H_2O$.

1. Heated under the blow-pipe on charcoal, barium compounds give a white, infusible mass which glows when strongly heated.

2. Barium compounds give no indication in the borax bead.

3. Barium compounds moistened with hydrochloric acid give an apple-green colour to the Bunsen flame. This colour is very persistent and may persist long after other substances which produce coloured flames have been burnt in the wire.

4. Boil a solution of the barium salt with ammonium chloride (NH_4Cl) and cool.

(*a*) Add ammonium hydrate ($NH_4{\cdot}OH$)—no precipitate.

(*b*) Through a portion of the ammoniacal solution pass sulphuretted hydrogen (H_2S)—no precipitate.

*(*c*) To the rest of the solution add ammonium carbonate [$(NH_4)_2CO_3$]—white precipitate of barium carbonate ($BaCO_3$).

*(*d*) Filter the precipitate and dissolve it in dilute acetic acid ($CH_3{\cdot}COOH$).

*(*e*) To the solution add potassium chromate solution ($K_2{\cdot}CrO_4$)—a yellow precipitate of barium chromate ($BaCrO_4$) is thrown down. This precipitate is insoluble in acetic acid ($CH_3{\cdot}COOH$)—distinction from calcium and strontium.

*5. To a solution of a barium salt add calcium sulphate ($CaSO_4$)

solution—a white precipitate of barium sulphate ($BaSO_4$), insoluble in dilute mineral acids, is formed.

EXPT. 198.—**Strontium,** Sr.

Use strontium chloride or nitrate.

1. Heated under the blow-pipe on charcoal, strontium compounds give a white, infusible mass which glows when strongly heated.

2. Strontium compounds give no indication in the borax bead.

3. Strontium compounds moistened with hydrochloric acid give a brilliant crimson colour to the Bunsen flame. The colour quickly dies away.

4. Boil a solution of a strontium salt with ammonium chloride solution (NH_4Cl); cool.

(*a*) Add ammonium hydrate ($NH_4 \cdot OH$)—no precipitate.

(*b*) Through a portion of the solution pass sulphuretted hydrogen (H_2S)—no precipitate.

*(*c*) To the rest of the solution add ammonium carbonate solution [$(NH_4)_2CO_3$]—white precipitate of strontium carbonate ($SrCO_3$).

*(*d*) Filter the precipitate and dissolve it by pouring acetic acid ($CH_3 \cdot COOH$) over it.

(*e*) To the solution add potassium chromate solution (K_2CrO_4)—no precipitate (distinction from barium).

*(*f*) To this solution add calcium sulphate solution ($CaSO_4$)—a white precipitate of strontium sulphate forms at once or on standing (distinction from calcium). This precipitate of strontium sulphate may also be formed by warming a solution of a strontium salt with ammonium sulphate [$(NH_4)_2SO_4$].

EXPT. 199.—**Calcium,** Ca.

Use calcium chloride, $CaCl_2,6H_2O$.

1. Heated under the blow-pipe on charcoal, calcium compounds give a white, infusible mass which glows when strongly heated.

2. Calcium compounds give no indication in the borax bead.

3. Calcium compounds, moistened with hydrochloric acid, give a yellowish-red colour to the Bunsen flame. *Learn to distinguish this from the sodium flame by comparing the two flames.*

4. Boil a solution of the calcium salt with ammonium chloride (NH_4Cl).

(*a*) Add ammonium hydrate (NH_4OH)—no precipitate.

(*b*) Through a portion of the ammoniacal solution pass sulphuretted hydrogen (H_2S)—no precipitate.

*(*c*) To the rest of the solution add ammonium carbonate [$NH_4)_2CO_3$]—white precipitate of calcium carbonate ($CaCO_3$).

*(*d*) Filter off the precipitate and dissolve it by pouring acetic acid ($CH_3{\cdot}COOH$) over it.

*(*e*) To the solution add potassium chromate solution (K_2CrO_4)—no precipitate (distinction from barium).

*5. (*a*) To a solution of a calcium salt add ammonium oxalate solution [$(NH_4)_2C_2O_4$]. A granular precipitate of calcium oxalate (CaC_2O_4) is thrown down. Filter and dry the precipitate.

*(*b*) The dry calcium oxalate on ignition should—

(1) not blacken.

(2) give off an inflammable gas—carbon monoxide (CO).

(3) leave a residue of calcium carbonate ($CaCO_3$) which, with a dilute acid, effervesces, giving carbon dioxide gas (CO_2).

Calcium oxalate is insoluble in acetic acid ($CH_3{\cdot}COOH$), but soluble in dilute hydrochloric acid.

Expt. 200—**Examine the given substances for the presence of barium, strontium, and calcium.**

Summary

It will be seen from the foregoing tests for barium, strontium and calcium that—

(1) None of these metals is precipitated by ammonium hydrate or ammonium sulphide in the presence of ammonium chloride.

(2) All these metals are precipitated by ammonium carbonate, giving carbonates of the metals.

(3) The precipitated carbonates are soluble in acetic acid.

(4) Barium is precipitated as barium chromate in the presence of acetic acid, while the chromates of calcium and strontium are soluble in acetic acid.

(5) If barium is not present, strontium may be precipitated by calcium sulphate solution.

(6) If (1) barium is not precipitated as chromate, nor (2) strontium precipitated as sulphate, then, both these metals being absent, calcium may be precipitated as oxalate. (NOTE.—Both strontium and barium give insoluble oxalates, so they must either be removed or proved to be absent before using ammonium oxalate as a precipitant for calcium.)

Boil substance with ammonium chloride; add ammonium hydrate. After showing, in a portion of the solution, that no precipitate is formed with sulphuretted hydrogen, add ammonium carbonate to the rest of the solution. A white precipitate is formed. Filter. Dissolve the precipitate by pouring acetic acid over it on the filter paper.

These facts are summarised in the following table:

To a portion of the solution add potassium chromate. A yellow precipitate indicates the presence of BARIUM. Confirm by flame test.	If no precipitate is given with potassium chromate, divide the rest of the solution into two parts.	
	I. Add calcium sulphate solution. A white precipitate at once, or on standing, indicates the presence of STRONTIUM. Confirm by flame test.	II. Boil solution with ammonium sulphate. If a white precipitate is thrown down test it for strontium. To solution add ammonium oxalate; white precipitate indicates the presence of CALCIUM. Confirm by flame test.

Equations (Group V)

Barium

4 (*c*) $BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$

Barium chloride with Ammonium carbonate gives Barium carbonate and Ammonium chloride

(*d*) $BaCO_3 + 2CH_3{\cdot}COOH$

Barium carbonate with Acetic acid

$= (CH_3{\cdot}COO)_2Ba + CO_2 + H_2O$

gives Barium acetate and Carbon dioxide and Water (*e*) $(CH_3{\cdot}COO)_2Ba + K_2CrO_4 = BaCrO_4 + 2CH_3{\cdot}COOK$

Barium acetate and Potassium chromate give Barium chromate and Potassium acetate

5 $BaCl_2 + CaSO_4 = BaSO_4 + CaCl_2$

Barium chloride and Calcium sulphate give Barium sulphate and Calcium chloride

Strontium

4 (*c*) $SrCl_2 + (NH_4)_2CO_3 = SrCO_3 + 2NH_4Cl$

Strontium chloride and Ammonium carbonate give Strontium carbonate and Ammonium chloride

(*d*) $SrCO_3 + 2CH_3\ COOH = (CH_3{\cdot}COO)_2Sr + CO_2 + H_2O$

Strontium carbonate and Acetic acid give Strontium acetate and Carbon dioxide and Water

(*e*) $(CH_3{\cdot}COO)_2Sr + CaSO_4 = SrSO_4 + (CH_3{\cdot}COO)_2Ca$

Strontium acetate and Calcium sulphate give Strontium sulphate and Calcium acetate

Calcium

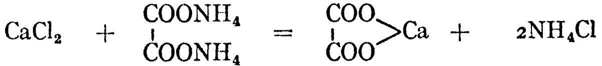
4 (*c*) $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$

Calcium chloride and Ammonium carbonate give Calcium carbonate and Ammonium chloride

(*d*) $CaCO_3 + 2CH_3{\cdot}COOH = (CH_3{\cdot}COO)_2Ca + CO_2 + H_2O$

Calcium carbonate and Acetic acid give Calcium acetate and Carbon dioxide and Water

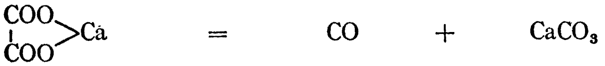
5 (*a*)



$$CaCl_2 + \begin{array}{l}COONH_4\\ \mid\\ COONH_4\end{array} = \left.\begin{array}{l}COO\\ \mid\\ COO\end{array}\right>Ca + 2NH_4Cl$$

Calcium chloride and Ammonium oxalate give Calcium oxalate and Ammonium chloride

(*b*)



$$\left.\begin{array}{l}COO\\ \mid\\ COO\end{array}\right>Ca = CO + CaCO_3$$

Calcium oxalate on heating gives Carbon monoxide and Calcium carbonate

DEMONSTRATION 44

SYSTEMATIC ANALYSIS OF A SINGLE SUBSTANCE

EXPT. 201.—**Identify the given salts A, B, C, etc.**

Preliminary Examination

1. **Describe the substance carefully.** Observe its colour, etc. Salts of Na, K, (NH_4), Mg, Bi, Ca, Sr, Ba, Zn, and Al are usually white unless the acid radical [*e g*. $(CrO_4)''$, $(MnO_4)''$, and $(MnO_4)'$] is coloured.

Salts of copper are often blue or green.
„ „ "ferrous" iron are often green.
„ „ "ferric" iron are often yellow or colourless.
„ „ chromium are often green or pink.
„ „ manganese are often pink.
„ „ nickel are often green.
„ „ cobalt are often red or pink.

Iodides, bromides, and sulphides are often coloured.

Notice if the substance is crystalline or amorphous, and also if it is soluble in water.

2. EXPT. 202—**Heat a little of the powdered substance dry in a small test-tube.**—Note carefully—

(1) What happens to the substance.
(2) If any gas is given out.
(3) If there is a sublimate or condensed vapour.
(4) The residue.

OBSERVATION.	INFERENCE.
1. (*a*) The substance fuses.	Many salts do this. If the substance is white and there is no change in colour, the substance may be salt of alkali or alkaline earth.
(*b*) Water is given out and condenses on the upper part of the tube.	Water of crystallisation or decomposition of an acid salt.
(*c*) The substance swells up (intumesces).	Borates, phosphates, alums.

Observation.	Inference.
2. *A gas is given out.*	
(*a*) **It is coloured.**	
Brown—turns ferrous sulphate black.	NO_2 from nitrates of heavy metals.
Brown—does not turn ferrous sulphate black.	Some bromides.
Greenish-yellow—notice its odour. (Iodide starch paper).	Chlorine from certain chlorides, chlorates and hypochlorites.
Violet—iodine—starch paper.	Some iodides
White—strongly acid.	Sulphur trioxide, some sulphates and bisulphates.
(*b*) **It is colourless, but has an odour.**	
Rotten eggs (lead acetate paper)	Some thiosulphates.
Burning sulphur (chromate paper).	Bisulphates, sulphides, sulphites and thiosulphates.
Sulphur dioxide and sulphuretted hydrogen.	Thiosulphates.
Ammonia (litmus, turmeric, smell, and rod moist with HCl).	Ammonium salts.
(*c*) **It is colourless and odourless.**	
(*a*) *Burns.*	
(1) Carbon monoxide.	Oxalates.
(2) Organic fumes.	Acetates, etc.
(*b*) *Supports combustion.*	
(1) Oxygen.	Some nitrates, chlorates, peroxides and other highly oxygenated compounds.
(2) Nitrous oxide (and water).	Ammonium nitrate.
(*c*) *Neither burns nor supports combustion.*	
(1) Turns lime-water milky.	Carbon dioxide from oxalates, carbonates, bicarbonates.
(2) Does not turn lime-water milky.	Nitrogen from ammonium nitrite and a few other substances.
3. *There is a sublimate or condensed vapour on the upper part of the tube.*	
(*a*) **It is colourless.**	Water of crystallisation, or acid salt or certain organic substances.
(*b*) **It is coloured.**	
Orange.	Antimony trisulphide.
Yellow. Smell of SO_2.	Sulphur, some sulphides, arsenious sulphide.
Yellow ; turns red on rubbing.	Mercuric iodide.

OBSERVATION.	INFERENCE.
White (accompanied by smell of ammonia). (If NH_3 is suspected, confirm with NaOH at once.)	Ammonium salts.
White (smell of garlic).	Arsenious oxide.
White.	Salts of mercury, etc.
Silver mirror. (Runs together into drops when rubbed.)	Mercury.
Black sublimate ; purple vapour.	Iodine.
Brown, oily drops (smell).	Bromine.
4. *The residue in the tube has changed colour.*	
Yellow when hot; white when cold.	Zinc.
Yellowish when hot; dirty white when cold.	Tin.
Orange to reddish-brown when hot; light yellow when cold.	Bismuth.
Yellow to reddish-brown, when hot; yellow when cold.	Lead.
Dark brown to black.	Iron, cobalt, nickel, manganese.
Black when hot; reddish when cold	Mercuric oxide, Fe_2O_3.
Black and charred.	Organic matter.
Reddish metallic-looking particles.	Reduced copper from (*e.g.*) copper acetate.

3. EXPT. 203.—**Treat with dilute hydrochloric acid.**

OBSERVATION.	INFERENCE.
A gas is evolved.	
(*a*) **It is coloured.**	
Brown (black colour with ferrous sulphate solution).	NO_2 from nitrites.
Brown (no black colour with ferrous sulphate).	Hypobromite.
Greenish-yellow (smell. Pot.-iodide-starch paper).	Chlorine from chlorates or hypochlorites. Some peroxides.
(*b*) **It is colourless but has an odour.**	
(1) Of sulphuretted hydrogen (lead acetate paper).	Some sulphides.
(2) Of burning sulphur (chromate paper).	Sulphur dioxide from a sulphite.
(3) Of burning sulphur with separation of yellow sulphur.	Thiosulphate.
(*c*) **It is colourless and odourless.**	
Turns lime-water milky.	Carbonates and bicarbonates.

N.B.—Any bicarbonate you would be given would be soluble in water. Add a solution of magnesium sulphate—no precipitate. Boil. White ppt. of $MgCO_3$—bicarbonate present. (See page 80.)

4. EXPT. 204.—**Treat a little of the substance with concentrated sulphuric acid.**—(Warm very cautiously at first.)

OBSERVATION.	INFERENCE.
Explosions in the tube.	Chlorate.
Coloured fumes are evolved—	
Brown—NO_2 ($FeSO_4$ test).	Nitrate or Nitrite.
Brown—bromine (accompanied by white fumes).	Bromide.
Violet—iodine (accompanied by white fumes).	Iodide.
White—dense acid fumes (NH_3 test).	Chloride.
Smell of vinegar.	Acetate.
Oxygen is evolved	Peroxides, chromates, etc
Gas burns (no blackening), accompanied by carbon dioxide	Oxalate.

5. EXPT. 205.—**Test separately for borate, fluoride, and silica.**

OBSERVATION.	INFERENCE.
(*a*) Put a little of the original substance on porcelain. Pour strong sulphuric acid on it. Mix well. Pour alcohol on the mixture Ignite the alcohol Stir the mixture when the alcohol is burning. It burns with a green flame.	Borate present.
(*b*) Mix some of the substance with a little sand. Pour sulphuric acid on the mixture and warm gently Dip a glass rod in water and plunge the rod into the mouth of the tube. Hold the rod in the vapour. Do not touch the hot acid A gelatinous blob forms on the end of the rod.	Fluoride present.
(*c*) Mix some of the substance with calcium fluoride and put it in a leaden capsule. Pour strong sulphuric acid on the mixture and warm. Suspend a drop of water on a watch glass and cover the capsule with it. A gelatinous blob forms on the watch-glass where the drop of water was.	Silica or a silicate present.

EXPT. 206.—**Intimately mix some of the original substance, finely powdered, with fusion mixture, and put a little in a hole scooped out of charcoal. Heat this under the mouth blow-pipe.**

OBSERVATION.	INFERENCE.
The substance decrepitates.	Many crystalline salts.
The substance deflagrates.	Nitrates, chlorates, etc.
A garlic-smelling vapour. It is white.	Arsenic.
White vapours.	Many compounds.
Residue is coloured, but with no bead of metal—	
Coloured incrustation, no bead.	Salts of Cu, Fe, Cr, Mn, Ni, Co.
White fume with garlic odour.	Arsenic.
,, fume with no garlic odour.	Antimony, etc.
Yellow when hot, white when cold.	Zinc, Tin.
Reddish-brown (possibly a few metallic particles)	Cadmium.
Metallic bead, with or without incrustation—	
Bright white bead—no incrustation.	Silver.
Red metal—no incrustation.	Copper.
White malleable metal marks paper—yellow incrustation.	Lead.
Soft white, malleable bead. Incrustation is yellow when hot, dirty white when cold	Tin
White brittle bead Incrustation orange-coloured when hot, pale yellow when cold.	Bismuth.
Residue is white It may fuse and sink into the charcoal.	Salts of alkali metals.
Residue is white and glows	Alkaline earths, alumina.
Residue is yellow when hot and glows	Zinc oxide, Tin oxide.

EXPT. 207.—**Moisten the white residue with two drops of cobalt nitrate or chloride and again heat under the blow-pipe.**

OBSERVATION.	INFERENCE
Residue is pink.	Magnesium present.
Residue is blue.	Aluminium present.
Residue is green.	Zinc present.

N.B.—Do not forget that phosphates and borates may fuse up into beads and dissolve cobalt oxide, giving a blue colour. The above residues should not be "beads." Confirm the metals in the wet way.

EXPT. 208.—**Apply borax bead test.** (See Expt. 169, page 155.)

The colour of the bead—

IN THE INNER OR REDUCING FLAME IS	IN THE OUTER OR OXIDISING FLAME IS	INDICATES THE PRESENCE OF
Red when cold (addition of tin helps the result).	Green when hot Blue when cold	Copper.
Yellowish when hot Olive green when cold	Brownish-red when hot Light yellow when cold	Iron.
Green.	Green	Chromium.
Blue.	Blue.	Cobalt.
Grey, or opaque, and black	Cherry-red when hot Brownish when cold	Nickel.
Colourless.	Amethyst (violet).	Manganese.
Opaque.	Opaque.	Too much substance. Start again.
White.	White.	Many substances.
White skeleton.	White skeleton.	Silica.

EXPT. 209.—**Apply the flame test.** Clean your platinum wire by alternately putting it in hydrochloric acid and the clear Bunsen flame.

Moisten some of your substance with hydrochloric acid, dip the platinum wire in it and put it in the flame. It may be found advantageous to use the blow-pipe flame for these flame tests.

Note that easily reducible metals will corrode your platinum wire.

THE COLOUR OF THE FLAME IS	INDICATION.
Brilliant golden-yellow.	Sodium.
Green (with HCl) ; blue alone.	Copper.
Green	Borates.
Yellowish-green—very persistent.	Barium.
Violet—looks red through cobalt blue glass.	Potassium.
Crimson—flashes up quickly and does not persist.	Strontium.
Dull reddish-yellow.	Calcium.
Pale blue flame.	Many substances.
Smell of garlic ; wire corroded.	Arsenic.

To distinguish clearly between calcium and sodium, take salts from your bench and compare the flame given by a known substance with that given by the substance under examination.

This " comparison method " is always permissible.

SYSTEMATIC EXAMINATION IN THE WET WAY

EXPT. 210.—**Examination for bases.**

The substance given is a solid.

Finely powder the solid. Try to dissolve it in water—first cold, then hot.

If insoluble in water add *dilute hydrochloric acid.*

If it does not dissolve in the cold, heat.

If insoluble in dilute hydrochloric acid try *strong hydrochloric acid.* Heat if necessary.

See if the substance is soluble in *nitric acid.* Finally try *aqua regia* (a mixture of nitric and hydrochloric acids ($HNO_3 : HCl : 1 : 3$).

If the substance is insoluble in the solvents given above, finely powder some of the substance and mix it intimately with sodium carbonate and then heat strongly with the foot blow-pipe till no more action takes place. Cool. Boil with water and filter. All the sodium salts of the acids are soluble in water, and the sodium salt of the acid radical of the given salt will be in the filtrate. Note that certain metals may come through as negative or acid radicals, *e.g.*, chromium as chromates, etc Examine by the tables given on pages 149–152, for the systematic examination for acid radicals.

The metallic portion of the salt will remain behind as insoluble carbonate or oxide. Examine residue for bases by adding dilute hydrochloric acid to the residue. If it is soluble in dilute hydrochloric acid proceed with the tables. If the residue is not soluble in dilute hydrochloric acid, dissolve it in dilute nitric acid.

If a liquid is given—

Smell it. Notice if it has the odour of sulphuretted hydrogen, sulphur dioxide, chlorine, etc. Test its action with litmus.

If it is *acid* it may be due to—

(1) A free acid.
(2) An acid salt.
(3) A normal salt which gives an acid reaction.

If it is *alkaline* it may be due to—

(1) An hydroxide.
(2) A normal salt of certain weak acids, *e.g.*, carbonates or borates.

Test specially for hydroxides. They give the following reactions: (1) With an alcoholic solution of phenolphthalein a red coloration is obtained. (2) Ferric chloride solution produces a brown precipitate of ferric hydroxide. (See Expt. 54, page 57.) Some carbonates give these tests, but if the solution gives no test for any acid radical, but gives the above tests, the presence of an *hydroxide* is indicated. (See page 57.)

Test specially for peroxides. (1) With HCl they give chlorine, (2) with sulphuric acid they give oxygen, (3) add a little dilute sulphuric acid and then about ½ inch layer of ether. Add two drops of potassium chromate or bichromate solution, and shake the tube gently. Keep the tube cool. A blue coloration in the ethereal layer indicates the presence of a peroxide.

Test especially for water. If *neutral* the substance may be water. Many salts in solution give a neutral reaction. Evaporate to dryness on a water-bath.

If the solution was neutral and no residue is left the substance was water or hydrogen peroxide.

If the solution was acid and leaves no residue the substance was a free acid and the acid was volatile.

Otherwise a residue will remain and this may be examined systematically by the tables given below.

To the solution add dilute hydrochloric acid.

<table>
<tr>
<td rowspan="5">White precipitate. Examine by TABLE No. I.</td>
<td colspan="5">If the preliminary tests indicated the presence of arsenic, manganese, chromium, or antimony, warm the solution with sulphurous acid. Boil off any excess of SO_2 and pass sulphuretted hydrogen.
If above metals were not indicated, there is no necessity to pass sulphur dioxide or boil with sulphurous acid before passing sulphuretted hydrogen.
After passing sulphuretted hydrogen filter off any precipitate. Wash it.</td>
</tr>
<tr>
<td rowspan="4">Coloured precipitate. Examine by TABLE No. II.
A white precipitate may be sulphur. (Confirm.)</td>
<td colspan="4">If no precipitate with H_2S, take a fresh portion of the solution. Boil with SO_2 (if necessary). Boil off excess of SO_2. To a small portion add two drops of nitric acid, warm, cool, then add potassium ferrocyanide No blue precipitate. *Iron is absent.* Throw this down the sink. To another small portion add more nitric acid. Boil Boil some ammonium molybdate solution with nitric acid. Add the two solutions together. Boil again. A yellow precipitate indicates presence of *phosphoric acid.* To rest of solution add ammonium chloride; boil, cool, add ammonium hydrate, filter.</td>
</tr>
<tr>
<td rowspan="3">Precipitate In absence of phosphoric acid. Examine by TABLE No. III.
Phosphoric acid present. Examine precipitate by TABLE No. IIIA.</td>
<td colspan="3">No precipitate. Pass sulphuretted hydrogen through a little of the solution If a precipitate forms, pass the gas through the rest of the solution.</td>
</tr>
<tr>
<td rowspan="2">Precipitate. Examine by TABLE No. IV.</td>
<td colspan="2">No precipitate. To the rest of the solution, add ammonium carbonate.</td>
</tr>
<tr>
<td>A white precipitate. Examine by TABLE No. V.</td>
<td>No precipitate. Examine the original substance for Na, K, Mg, (NH_4).</td>
</tr>
</table>

If the preliminary tests have shown the presence of oxalic, acetic, hydrofluoric or boric acids, evaporate to dryness with nitric acid after Group II.

TABLE NO. I.—FIRST GROUP

To a portion of the precipitate add ammonium hydrate.

Precipitate dissolves. Silver is present. Add dilute nitric acid. The precipitate is re-formed—indicates the presence of **SILVER.**	Precipitate is turned black. Dry the precipitate. Mix with dry sodium carbonate and a little potassium nitrate Heat the mixture in a bulb tube. Mirror on the upper part of tube indicates the presence of **MERCURY(OUS)**	No apparent action with ammonium hydrate. Boil rest of precipitate with water; cool; a crystalline precipitate settles down. **LEAD** is present. Confirm by tests. (See Expt. 177, page 164.)

TABLE NO. II.—SECOND GROUP

Wash the precipitate with H_2S water. Notice its colour. If yellow or brown, warm with yellow ammonium sulphide solution. If the precipitate is black—*cadmium, arsenic, antimony* and *tin* are absent.

<table>
<tr><td colspan="3">The precipitate is insoluble in ammonium sulphide.</td><td colspan="3">The precipitate is soluble in ammonium sulphide. To the solution add concentrated hydrochloric acid and boil.</td></tr>
<tr><td rowspan="3">The precipitate is yellow; indicates presence of
CADMIUM.
Confirm.</td><td colspan="2">Precipitate is black.
Take a fresh portion and boil with 50 per cent. nitric acid.</td><td rowspan="3">Yellow precipitate insoluble in strong hydrochloric acid indicates the presence of
ARSENIC.
Confirm by tests on page 174, Expt. 184.</td><td colspan="2">No precipitate, or the precipitate first formed is again dissolved. To solution add a small piece of platinum foil and some zinc in contact with it.</td></tr>
<tr><td rowspan="2">Precipitate is insoluble. It may turn grey or white. Dry the precipitate.
Mix with dry sodium carbonate and nitre and heat in a bulb tube.
Metallic mirror indicates the presence of
MERCURY(IC).
Note Be sure that you are not mistaking a precipitate of sulphur for mercuric sulphide. If the above confirmatory test is given, the residue was certainly mercuric sulphide. If the residue does not give the test for mercury, it was probably sulphur, possibly $PbSO_4$ if lead is present.</td><td>Precipitate is soluble. Divide into two parts A and B.</td><td rowspan="2">Black stain on the platinum indicates the presence of
ANTIMONY.</td><td rowspan="2">No black stain on platinum.
Dissolve residue completely in hydrochloric acid. To solution add mercuric chloride solution; white precipitate turning grey on warming indicates the presence of
TIN.</td></tr>
<tr><td>A. Add dilute sulphuric acid. White precipitate soluble in ammonium acetate indicates the presence of
LEAD.
B. Add ammonium hydrate.
(*a*) White precipitate soluble in hydrochloric acid; but reprecipitated on large dilution indicates the presence of
BISMUTH.
(*b*) The solution turns a bright blue colour. This indicates the presence of
COPPER.</td></tr>
</table>

TABLE NO. III.—GROUP III (PHOSPHATES ABSENT)

Precipitate consists of the hydroxide of aluminium, iron, or chromium.

It is *white*. Dissolves in NaOH. Confirm by charcoal test. (See Expt. 190 (1), page 182.) ALUMINIUM present.	It is *reddish-brown*. Dissolve precipitate in dilute hydrochloric acid. To solution add potassium ferrocyanide. Blue precipitate indicates the presence of IRON. Test the original substance to determine whether the iron existed in the ferrous or ferric state. (See Expt. 188, page 180.)	A *green* precipitate indicates chromium. Mix precipitate with fusion mixture and a little solid caustic soda and heat under blow-pipe on porcelain. A yellow mass. Indicates presence of CHROMIUM. Confirm. (See Expt. 189, page 182).

GROUP III (PHOSPHATES PRESENT)

If phosphoric acid is present the precipitate may consist of the phosphates of Fe, Al, Cr; Co, Ni, Mn, Zn; Ca, Ba, Sr; or Mg, or the hydroxides of Fe, Al or Cr.

It will be noticed that all these give some test either in the flame or in the borax bead by which they may be detected and by which they should have been indicated in the preliminary examination.

1. *The precipitate is coloured.* It may be—

(1) *Iron* (yellowish)—already tested for; (2) *chromium* (green), apply chromate test by fusion; (3) *manganese,* apply manganate test by fusion; (4) and (5) *cobalt and nickel*—bead test.

2. *The precipitate is white.* It may be *calcium, strontium* or *barium*—apply flame test; *aluminium, zinc* or *magnesium*—charcoal and cobalt nitrate test.

3. If phosphoric acid is present and *there is no precipitate* when ammonium chloride and ammonium hydrate are added, test the original substance for sodium, potassium and ammonium.

NOTE.—It is necessary to modify the method of analysis when phosphates are present because, when ammonium hydrate is added to the solution which has been boiled with ammonium chloride after Group II., the phosphates of iron, aluminium, chromium, cobalt, manganese, nickel, zinc, barium, strontium, calcium and magnesium are partially or completely precipitated as well as the hydroxides of iron, aluminium and chromium.

In order to eliminate the phosphoric acid and so render it possible to analyse the solution for metals in the usual way, advantage is taken of the fact that "ferric," aluminium and chromium phosphates are insoluble in acetic acid, while the phosphates of the other metals are soluble in acetic acid.

The details of the process by which this is carried out are given in the next table—No IIIA.

TABLE NO. IIIA.—GROUP III (PHOSPHATES PRESENT)

SECOND METHOD:—

Dissolve precipitate in the least possible quantity of dilute hydrochloric acid. Then neutralise the excess of hydrochloric acid with solid sodium carbonate until a trace of curdy precipitate appears. Then add one drop of dilute hydrochloric acid to remove curdiness. Now add sodium acetate solution and acetic acid. Warm and filter the solution and, while still hot, wash the precipitate with hot water.

Precipitate. Examine for iron, chromium and aluminium.	Neutralise some ferric chloride solution (with ammonium hydrate) and add drop by drop to the filtrate till no more precipitate appears and the supernatant liquid is red Heat and filter hot, wash with hot water.				
	Precipitate Reject.	Warm the filtrate with concentrated ammonium chloride and add ammonium hydrate solution.			
		Precipitate. Examine by TABLE III.	Through filtrate pass sulphuretted hydrogen.		
			Precipitate Examine by TABLE IV.	If no precipitate, warm with ammonium carbonate.	
				White precipitate. Examine by TABLE V.	No precipitate; add disodium, hydrogen phosphate; white precipitate. MAGNESIUM present. Confirm by charcoal test. (See Expt. 174(2), page 160.)

TABLE NO. IV.—GROUP IV

<table>
<tr><td colspan="2">The precipitate is black</td><td colspan="2">The precipitate is not black.</td></tr>
<tr><td colspan="2">Examine by bead tests.</td><td colspan="2">Dissolve the precipitate in dilute hydrochloric acid. Add sodium hydrate. A precipitate is formed.</td></tr>
<tr><td>Blue bead in both oxidising and reducing flames indicates the presence of
COBALT.</td><td>Violet (hot) red (cold) in oxidising flame, grey in the reducing flame, indicates the presence of
NICKEL.</td><td>(1) Soluble in excess of caustic soda
Pass sulphuretted hydrogen through the solution A white precipitate indicates the presence of
ZINC.</td><td>(1) Insoluble in excess of caustic soda.
Fuse the precipitate with sodium carbonate and caustic soda —a green mass indicates the presence of
MANGANESE.</td></tr>
</table>

TABLE NO. V.—GROUP V

White precipitate. Pour acetic acid over the precipitate on the filter paper.

<table>
<tr><td rowspan="2">To a portion of the solution add potassium chromate. A yellow precipitate indicates the presence of
BARIUM.
Confirm by flame test.</td><td colspan="2">If there is no precipitate with potassium chromate divide the rest of the solution in two parts.</td></tr>
<tr><td>I. Add calcium sulphate solution. A white precipitate after some time indicates the presence of
STRONTIUM.
Confirm by flame test.</td><td>II. Boil the solution with ammonium sulphate (white precipitate; test for strontium).
To solution add ammonium oxalate. White precipitate indicates the presence of
CALCIUM.
Confirm by flame test.</td></tr>
</table>

IMPORTANT

Write out your analysis in *tabular form.*

When you have finished your analysis write *at the end* of your report what you have found.

PART II

DETERMINATION OF EQUIVALENT WEIGHTS AND SIMPLE VOLUMETRIC ANALYSIS

Equivalent Weights

The equivalent weight of an element is the NUMBER of parts by weight of that element which will combine with or replace one part by weight of hydrogen.

It is not possible to cause certain elements to combine with hydrogen or to replace it. But practically all the elements combine with oxygen.

Now, by the first definition, the equivalent weight of oxygen is EIGHT, because eight parts by weight of oxygen combine with one part by weight of hydrogen to form nine parts of water.

Therefore if we find how many parts by weight of an element combine with eight parts by weight of oxygen we simultaneously find out how much of that element *would combine with one part by weight of hydrogen if it could do so, i.e.,* we find the equivalent weight of the element.

The word " parts " is used in the above because it is general, but we could use *any* unit of *weight,* and so the definition would read :

" The equivalent weight of an element is the *number* of grams of that element which will combine with or replace one gram of hydrogen or eight grams of oxygen."

In the following discussions and experiments on equivalents this definition will be employed, but it must be clearly understood that any unit of weight may be employed. The gram is used for convenience.

The equivalent weight is a NUMBER, not a quantity.

DEMONSTRATION 45

DETERMINATION OF EQUIVALENT WEIGHTS

EXPT. 211.—**Determination of the equivalent weight of a metal.**—METHOD No. 1.—By measuring the volume of hydrogen evolved when a weighed quantity of the metal is treated with dilute acid.

The apparatus described in Expts. 46, 76, Figs. 44, 53 (*a*), and 53 (*b*), may be employed.

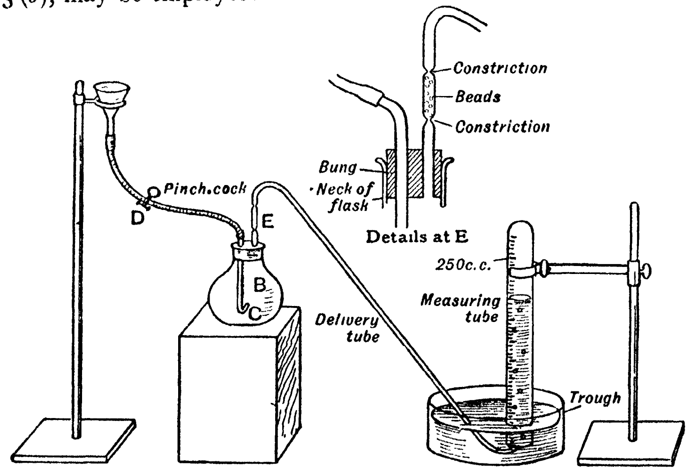


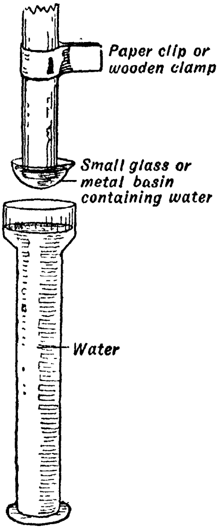
FIG. 67.

The apparatus described in Fenton's "Outlines of Chemistry" gives excellent results. It is shown in Fig. 67.

Weigh the metal in a watch glass and put it in the bottle, *B*. Run boiled water through the funnel until the whole apparatus is completely filled with water and not a bubble of air is left in it.

Shut the pinch-cock at *D*. Pour strong hydrochloric acid into the funnel and, having placed the measuring cylinder or gas jar over the end of the delivery tube, open the pinch-cock and allow the strong acid to run into the flask. It flows in at *C* and makes dilute acid when it mixes with the water in the flask. The dilute acid acts upon the metal and hydrogen is evolved. It passes into the graduated jar. Gas is prevented from escaping up the tube *C* by turning the end of *C* upwards; *C* should reach nearly to the bottom of the flask. Fragments of metal are prevented from passing along the delivery tube by the glass beads at *E*, details of which are shown at the right of the diagram. When the action ceases a steady stream of water is passed through the apparatus in order to sweep out the last bubbles of hydrogen.

Hold the measuring cylinder in a wooden clamp and place a small glass or metal bowl under its end (Fig. 68). Lift the cylinder and bowl out of the trough together and transfer to a hydrometer jar containing water (Fig. 69). Now release the little bowl and let the measuring tube sink until the level of water inside and outside the tube is the same. This eliminates a correction due to the column of water. Read off the volume of the gas. Read the atmospheric pressure from the barometer in the balance room. Find the temperature of the laboratory and the pressure of aqueous vapour at that temperature.


Paper clip or wooden clamp
Small glass or metal basin containing water
Water

FIGS. 68 and 69.

Data :—

Weight of watch glass and metal = m grams.
„ „ „ „ alone = m' „
∴ „ „ metal = $(m-m')$ „
Observed volume of gas = v c.c.
Observed temperature of laboratory = $T°$ C.
Pressure of aqueous vapour at $T°$ C. = b mm. Hg.
Barometric pressure = B mm. Hg.

Volume of gas at N.T.P. $= v \times \left(\frac{B-b}{760} \times \frac{273}{273+T}\right)$ c.c. (*vide* page 52).

But weight of 1 c.c. of hydrogen at N.T.P. $= \frac{1}{11,111}$ grams.

$\therefore$ Weight of hydrogen evolved

$$= \left(v \times \frac{B-b}{760} \times \frac{273}{273+T} \times \frac{1}{11,111}\right) \text{ grams.}$$

$$= x \text{ grams (suppose).}$$

Weight of metal required to evolve x grams of hydrogen is $(m-m')$ grams.

$\therefore$ Weight of metal required to evolve one gram of hydrogen is $\frac{(m-m')}{x}$ grams $=$ . . . grams.

$\therefore$ *Required equivalent weight of zinc is . . .* *Ans.*

DEMONSTRATION 46

DETERMINATION OF EQUIVALENT WEIGHTS—*continued*

EXPT. 212.—METHOD NO. 2 (DIRECT OXIDATION METHOD).—**To determine the equivalent weight of magnesium.**—Weigh a crucible and lid.

Into the crucible place about half a gram of magnesium ribbon and weigh again. Remove the crucible, etc., from the balance and put the weights back in order.

Put the crucible on a tripod and heat it. The magnesium begins to oxidise; continue heating with the lid on. Finish heating with the lid removed. Cool in a desiccator and weigh again.

Data :—

Weight of crucible and lid = m grams.
Weight of crucible lid and magnesium = m' „
∴ Weight of magnesium = $(m'-m)$ „
Weight of crucible lid and magnesium oxide after experiment = m'' „
∴ Weight of oxygen = $(m''-m')$ „
Weight of magnesium which combines with $(m''-m')$ grams of oxygen = $(m'-m)$ „
∴ Weight of magnesium which combines with 1 gram of oxygen = $\dfrac{(m'-m)}{(m''-m')}$ „
∴ Weight of magnesium which combines with 8 grams of oxygen = $\dfrac{(m'-m)}{(m''-m')} \times 8$ „
∴ *Required equivalent weight of magnesium is* . . . *Ans.*

EXPT. 213.—METHOD NO. 3.—**Equivalent weight of tin.**—Weigh out about 0·75 gram of tin in a crucible. Place the crucible aslant on a clay triangle on a tripod (Fig. 35, page 38).

Drop a few drops of nitric acid upon the tin. Continue adding nitric acid until all action ceases. Warm the crucible, starting from the outside edge (Expt. 35, page 38), and continue heating till no more oxides of nitrogen are evolved. Heat strongly for two minutes; cool, weigh.

The tin will have been converted into tin oxide, $Sn + O_2 = SnO_2$. The oxygen is supplied by the nitric acid.

Hence calculate in the equivalent weight of tin.

EXPT. 214.—METHOD NO. 4.—**Equivalent weight of copper.**—Treat about 0·5 to 0·75 gram of copper with nitric acid as in method No. 3. Be very cautious and see that no spurting occurs. Copper nitrate will first be formed. Heat from the outside edge as before. The copper nitrate will decompose into cupric oxide, CuO. Weigh the residue and calculate the equivalent weight of copper.

Do not heat the copper oxide too strongly or it will undergo partial decomposition. If you wish to save loss by spurting put the crucible lid on *upside down*.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

INTRODUCTION TO VOLUMETRIC ANALYSIS

It has been explained that the equivalent weight of an element is the NUMBER of grams of that element which will combine with or replace one gram of hydrogen—or eight grams of oxygen (page 215).

Similarly, the equivalent weight of an acid is the NUMBER of grams of that acid which contains one gram of hydrogen replaceable by a metal.

Also, the equivalent weight of a base is the NUMBER of grams of that base which will neutralise the quantity of any acid which contains one gram of hydrogen replaceable by a metal (*i.e.,* the equivalent weight of the acid measured in grams, or the gram-equivalent of the acid).

And the equivalent weight of an oxidising agent is the NUMBER of grams of that oxidising agent which contains sufficient oxygen (capable of being used for purpose of oxidation) to oxidise one gram of hydrogen.

Oxygen which can be used for the purpose of oxidation is called **available oxygen.**

Thus the equivalent weight of an oxidising agent is the NUMBER of grams of that oxidising agent which contain eight grams of "available oxygen."

In the same way the equivalent weight of a ferrous salt is the NUMBER of grams of that salt which contain sufficient ferrous iron to require eight grams of oxygen to oxidise it from the ferrous to the ferric state and so on.

A few explanatory examples will make the fundamental principles more clear.

One gram of hydrogen combines with 35·5 grams of chlorine to form 36·5 grams of hydrochloric acid. All this hydrogen is replaceable by a metal. Therefore the equivalent weight of hydrochloric acid is 36·5.

Again in sulphuric acid [$(H_2SO_4)=2+32+64$] we have 98 grams of acid in which all the hydrogen is replaceable by a metal.

But 98 grams of the acid contain 2 grams of replaceable hydrogen, therefore the equivalent weight of sulphuric acid $\frac{98}{2}=49$, *i.e.,* the number of grams of the acid which contain one gram of hydrogen replaceable by a metal.

The **basicity** of an acid is the number of atoms of replaceable hydrogen contained in one molecule of the acid. (See Demonstration 17, page 79.)

Hence the basicity of hydrochloric acid is one.
" " " " sulphuric " " two.
" " " " carbonic " " two.
" " " " phosphoric " " three.

or generally, basicity $= \frac{\text{molecular weight}}{\text{equivalent weight.}}$

Similarly, $\frac{\text{molecular weight}}{\text{basicity}} =$ equivalent weight.

The substance potassium bisulphate contains one atom of replaceable hydrogen in a molecule, therefore the equivalent weight of potassium bisulphate will be, from its formula,

$$KHSO_4 = 39 + 1 + 32 + 64 = 136.$$

For a **base** we have a similar reasoning.

If caustic soda is allowed to interact with hydrochloric acid the reaction which takes place may be represented by the equation

$$\underset{(23+16+1)}{NaOH} + \underset{(1+35{\cdot}5)}{HCl} = NaCl + H_2O$$

i.e., 40 grams of caustic soda is the amount of caustic soda required to neutralise 36·5 grams of hydrochloric acid.

But 36·5 grams of hydrochloric acid contain one gram of replaceable hydrogen.

∴ the equivalent weight of caustic soda is 40.

Again $$\underset{\underbrace{(46+12+48)}_{106}}{Na_2CO_3} + \underset{\underbrace{(2\times 36{\cdot}5)}_{73}}{2HCl} = 2NaCl + H_2O + CO_2$$

From the equation we see that 106 grams of sodium carbonate require 73 grams of hydrochloric acid for their complete decomposition. But 73 grams of hydrochloric acid contain 2 grams of replaceable hydrogen.

∴ 106 grams of sodium carbonate require two equivalents of hydrochloric acid to react with them.

∴ the equivalent weight of sodium carbonate is $\frac{106}{2} = 53$.

The equivalent weight of any substance can be worked out in terms of hydrogen.

NOTE.—Some bodies may function in two different ways and under such circumstances may have two different equivalent weights—according to which particular duty the body is performing at the time, *e.g.*, formic acid, $H \cdot COOH$, contains two atoms of hydrogen. Only one of these is capable of being replaced by a metal. Therefore as an acid its equivalent weight will be $(1+12+32+1)=46$.

On the other hand formic acid can behave as a reducing agent and, when oxidised, forms water and carbon dioxide, $H \cdot COOH + O = CO_2 + H_2O$.

From the equation it can be seen that 46 grams of formic acid require 16 grams of oxygen for their complete oxidation.

But the equivalent weight will be number of grams which requires the amount of oxygen required by one gram of hydrogen, *i.e.*, eight grams of oxygen.

$\therefore$ the equivalent weight of formic acid, as a reducing agent, is $\frac{46}{2}=23$.

Conditions necessary that Volumetric Analysis may be possible

It will be seen that, taking advantage of this system of equivalents, we have a means of performing quantitative analysis in solution (VOLUMETRIC ANALYSIS) providing that—

1. We know exactly what chemical action is proceeding, and can represent it by a chemical equation. If then we know the amount of *one* of the substances which has taken part in the reaction, the amounts of the *other* substances which take part in the reaction can be calculated.
2. The reaction proceeds to entire completion under easily procurable circumstances.
3. We have a means of determining exactly when the definite action is complete, *i.e.*, a means of determining the " end point " of the reaction.
4. The reaction should be definite and complete over a fairly wide range of concentration.

Indicators

The substances used to mark the " end point " of a reaction are called "indicators." They are substances which do not affect the reaction which is proceeding, but which give a characteristic colour with one of the bodies taking part in the reaction. *e.g.* : If a drop of phenolphthalein is put into some dilute hydrochloric acid the solution is colourless. Add caustic soda slowly.

So long as there is acid present the caustic soda is destroyed, but as soon as the acid is all neutralised the caustic soda is in excess and immediately reacts with the indicator, phenolphthalein, and produces a pink colour in the solution.

Some indicators change from one colour to another, *e.g.*, blue litmus is turned red by an acid. If you make a habit of always putting the acid in the burette you will get accustomed to telling when the colour changes from blue to pink. This is an advantage, so make a practice of always putting your acid in the burette and your caustic alkali or carbonate in the beaker.

The commoner indicators are :—

Indicator	Conditions for use.	Acid.	Alkaline.
Litmus.	Use for mineral acids and oxalic acid. Unreliable in presence of carbon dioxide	Pink.	Blue.
Methyl-orange.	It is itself an acid. Use as little as possible, and always add a constant amount. Not affected by CO_2 or H_2S. Use for stronger acids.	Pink.	Yellow.
Phenolphthalein.	Dissolved in dilute alcohol. Do not use for carbonates or ammonium compounds. Use with weak acids, but the acid used must be stronger than phenolphthalein (includes most organic acids). The base used must be strong, *e g.*, NaOH, $Ba(OH)_2$ etc. Carbonates, phenol, and ammonium salts give unreliable results.	Colourless	Pink.

For notes on the use of indicators, see Demonstration 47, page 229.

Note to Demonstrators.

The above indicators may be made up as follows :—

Litmus.—Digest 50 grams of litmus with 250 c.c. of hot water. Stand for twenty-four hours, filter. Add 200 c.c. of 50 per cent.

alcohol (rectified spirits) and make up to 500 c.c. with distilled water.

Methyl-orange.—Dissolve 1 gram of methyl-orange (Tropaeolin D.) in a little methylated spirits or rectified alcohol. Make up to one litre with 50 per cent. methylated spirits or 50 per cent. alcohol.

Phenolphthalein.—Dissolve 2 grams of phenolphthalein in 50 c.c. of rectified spirits (warm if necessary on a water-bath). Make up to 500 c.c. with 50 per cent. rectified spirits.

STANDARD SOLUTIONS

If a gram-equivalent weight of a substance is dissolved in water and made up to a litre (1,000 c.c.), the solution is said to be "normal," *e.g.*, normal sodium hydrate contains 40 grams of sodium hydrate (NaOH) in one litre of *solution* (not one litre of solvent).

Normal sulphuric acid contains $\frac{98}{2}$, *i.e.*, 49 grams of sulphuric acid in one litre of solution.

It will be seen from the above that one litre of a normal solution of any strong acid will just neutralise one litre of a normal solution of any strong base.

(The word "strong" is inserted because actions between weak acids and bases are incomplete, but at this stage of your study we are not concerned with weak acids and bases.)

In other words, normal solutions of acids and bases are inter-equivalent.

A solution which contains $\frac{1}{10}$ of a gram-equivalent of an acid or base or any substance in a litre of solution is said to be "decinormal."

Similarly, "centinormal" solutions contain $\frac{1}{100}$ of a gram-equivalent in a litre of solution, and "seminormal" solutions contain $\frac{1}{2}$ of a gram-equivalent in a litre of solution.

It is not always possible to arrange that our solutions are exactly normal or even an exact fraction or multiple of normal strength.

Although calculations are frequently more simple if the strengths of the solutions used are a fraction of the normal strength, this is by no means necessary, and we can use solutions of any known strength for the purpose of volumetric analysis.

Any solution the exact strength of which is known is a **standard solution**.

The strength or concentration of a solution is usually given by stating the number of grams of solute per c.c. or per litre, but it may be given in terms of normality.

e.g. : A solution whose strength is three-quarters normal strength is said to have a normality of $\frac{3}{4}N$.

It must be clearly understood that all *normal solutions* are *standard solutions*, but all standard solutions are not normal solutions.[1]

A " normal " solution is a standard solution of special strength.

The various strengths are often indicated by symbols, *e.g.*, N=normal, $\frac{N}{10}$=decinormal, etc.

The student is advised to work out his results in terms of " grams per c.c." or " grams per litre."

He should also state the result in terms of normality, which can always be calculated after the strength in grams per c.c. or per litre has been determined. Thus :—

$$\text{Normality} = \frac{\text{number of grams of substance in one litre of solution}}{\text{grame-quivalent weight of the substance}}.$$

∴ Normality = the number of "equivalents" of that substance dissolved in one litre of solution.

A **titration** is the process of using a solution of known strength in order to determine the strength of another solution

---

[1] This statement sometimes confuses the student. The difficulty is usually removed by giving some parallel case in terms of familiar objects, *e g.*, " All cats are animals, but all animals are not cats."

RULES to be observed when doing Volumetric Analysis.

1. Keep your bench clean and dry.

2. Wash out your burette and pipette with the solutions to be used in them respectively.

3. Pour acid or permanganate into the burette by means of a glass funnel. Remove the funnel from the burette before performing your experiment.

4. It is waste of time to try to fill the burette up to the zero mark; any point will do providing that it is on the scale, not above the level of your eye, and that there is sufficient solution present for your titration.

5. See that the burette is vertical, and place a piece of white paper behind it to throw up the scale.

6. See that the tap is tight and not leaking, and that it does not contain any air bubbles.

7. For transparent (colourless) liquids read the height of the bottom of the meniscus formed in the liquid in the burette or pipette.

For dark-coloured liquids (*e.g.*, potassium permanganate, etc.) read the upper edge of the meniscus.

8. A pipette is made to *deliver* the volume *stated* on the bulb. Let the pipette deliver its contents *slowly*, and just touch the surface of the liquid with the tip of the pipette when all the liquid has apparently been delivered from it.

DO NOT BLOW OUT THE LAST DROP OF LIQUID.

9. Use the INDEX FINGER (*not* the thumb) to close the open end of the pipette (Fig. 25, page 21).

10. For titrations to be done in the cold a white tea-cup is an excellent piece of apparatus.

For reactions requiring heat use an evaporating basin. If a beaker or flask is used for titrations put it on a piece of white paper or a white tile so that the colour-changes in the indicator may be shown up as clearly as possible.

11. Wash out the cup first with tap water and finally with distilled water between two titrations. Do not dry the cup after washing.

12. See that no drops splash on to the sides of the vessel, and see that no drops are left hanging on to the tap of the burette.

13. Thoroughly mix the solution during the titration by stirring with a glass rod. Do not splash. Wash the stirring rod between each titration.

14. Do not be satisfied with a titration of less than 10 c.c. As a rule try to arrange your titrations so that 20 to 25 c.c. of the solution have to be run in from the burette. The larger the amount used the smaller should be the percentage of error.

15. If you are not getting concordant results you are doing something wrong. Consult the demonstrator. All titrations should agree to at any rate the first place of decimals. Reject any titration which differs widely from the others.

Do not be satisfied until you have three concordant titrations. They should not differ by more than 0·05 c.c.

16. *Write down what you do when you do it, and immediately record the titrations in your note-book.*

17. Clearly state the units in which each measurement and calculation is made.

DEMONSTRATION 47

EXPT. 215.—**To find the strength of a solution of hydrochloric acid by means of a standard solution of sodium hydrate.**—Wash out your burette and tap with the given hydrochloric acid, and then, having dried the outside of the burette, clamp it in a stand and see that it is vertical.

Do not clamp the burette by metal directly. See that the inside of the clamp is padded with rubber, paper or cork, otherwise there is a chance of breaking the burette.

Place the burette in the stand in such a position that you can get your eye on exactly the same level as the graduation at which the liquid in the burette is standing, otherwise error due to "parallax" will be introduced.

Pour the acid into the burette by means of a glass funnel until the level of the liquid is near the top of the graduated part of the tube. Remove the glass funnel and see that the tap contains no air bubbles (Expt. 15, page 22).

You will see that the top of the liquid has the appearance of a half moon (this is called a meniscus) (Fig. 26, page 21). Read the graduation which makes a tangent with the curved surface of the

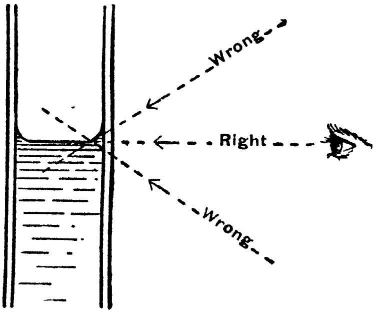


FIG. 70.

meniscus when looked at by the eye placed at the same level as the meniscus. If the eye is not at the same level as the meniscus, Fig. 70 shows how an error in reading is introduced by what is called "parallax."

Now wash out your pipette (20 c.c. or 25 c.c.) with the given caustic soda solution and throw the washings down the sink. Suck some of the caustic soda solution into the pipette until the level of the liquid is above the scratch on the stem. Remove the end from the mouth and at once close it with the INDEX (or FIRST) finger (Fig. 25, page 21). You will find it an advantage first to moisten the finger slightly. Allow caustic soda gradually to drip from the pipette by slightly lifting the finger, and continue doing so until the graduation on the stem of the pipette makes a tangent with the curved portion of the meniscus when viewed at eye level. Practise this until you acquire precision in filling the pipette correctly.

Now allow the caustic soda to run slowly from the pipette into a tea-cup. Add sufficient indicator to give a distinct colour, but always observe the following advice:—

1. Use as little indicator as possible. (Different students have different powers of detecting colours and intensity of colour, so it is impossible to give a general *rule* as to how much indicator will be requisite for any particular experiment; moreover, in different laboratories the indicators supplied are certain to vary in strength.)

2. Always use the same number of drops of the given indicator for a given set of titrations.

3. Always arrange your experiment in such a way that your colour change for a given indicator is observed in the same order, *e.g.*, in acid and alkali titrations always place the acid in the burette and the alkali in the tea-cup or beaker in which the reaction will take place. By doing this you will get accustomed to observing the litmus changing from blue to red, and thus become more expert in determining the end point. If desired, a pink-coloured solution may be kept for comparison.

Read your burette and note the entry in your note-book at once.

Now run in acid from the burette. Stir well, but *do not splash.*

Have your burette tap sufficiently near the liquid in the cup to prevent splashing and do not leave drops hanging on to the burette tap.

As soon as the neutral point is attained, read the burette again and write the reading in *your book at once* vertically below the reading taken before you started running in the acid.

Wash your *cup* and *stirring rod* first under the tap and then with distilled water.

Do not wash the pipette between different titrations in the same experiment.

Repeat the titrations until a constant result is obtained.

Write out your results in the following form:—

Volume of caustic soda used for each titration = 25 c.c.
Strength of caustic soda = 0·0038 gram NaOH per c.c.
Indicator used . . . . . litmus.

Titrations (against hydrochloric acid of known strength):—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Height of burette at beginning	~~0·20 c.c.~~	19·35 c.c.	3·00 c.c.	22·05 c.c.	5·40 c.c.
Ditto, at end ..	~~19·35 c.c.~~	38·35 c.c.	22·05 c.c.	41·05 c.c.	24·40 c.c.
Volume run in ..	~~19·15 c.c.~~	19·00 c.c.	19·05 c.c.	19·00 c.c.	19·00 c.c.

It will be observed that—

(1) Titrations 1 and 2 and titrations 3 and 4 were performed without refilling the burette.

(2) The first (trial) titration is clearly high; *reject* it entirely. This has been signified by drawing a neat line through it. From the above readings it is obvious that 19 c.c. of acid is the quantity required to neutralise 25 c.c. of the given caustic soda solution.

(3) Try the titration with other indicators, *e.g.*, methyl-orange or phenolphthalein. (In this case identical results should be obtained.)

Write out clearly the reasoning by which you calculate your result thus:—

19 c.c. of hydrochloric acid neutralise 25 c.c. of caustic soda solution containing 0·0038 gram of NaOH per c.c.

∴ Weight of caustic soda neutralised = 25 × 0·0038 grams.

From the equation representing the reaction

$$\underbrace{\underset{(35{\cdot}5+1)}{HCl}}_{36{\cdot}5} + \underbrace{\underset{(23+16+1)}{NaOH}}_{40} = NaCl + H_2O$$

We see that 36·5 grams of hydrochloric acid exactly neutralise 40·0 grams of sodium hydrate (caustic soda).

$\therefore$ Quantity of hydrochloric acid neutralised by 40 grams of caustic soda $\Big\} = 36{\cdot}5$ grams.

and quantity of hydrochloric acid neutralised by 1 gram of caustic soda $\Big\} = \frac{36{\cdot}5}{40}$ "

$\therefore$ Quantity of hydrochloric acid neutralised by $25 \times 0{\cdot}0038$ grams of caustic soda $= \frac{36{\cdot}5}{40} \times 25 \times 0{\cdot}0038$ grams.

But this is the quantity of hydrochloric acid in 19 c.c. of the given solution.

$\therefore$ Strength of the given solution of hydrochloric acid is

$$\frac{36{\cdot}5 \times 25 \times 0{\cdot}0038}{40{\cdot}0 \times 19} \text{ grams per c.c.}$$

Required result=0·004563 *gram* HCl *per c.c.* . . . *Ans.*

(What is the "normality" of the solutions used? See page 226).

This result in general terms becomes

$$\frac{\text{No. of c.c. of base used} \times \text{strength of base in grams per c.c.}}{\text{Equivalent weight of base}}$$
$$= \frac{\text{No. of c.c. of acid used} \times \text{strength of acid in grams per c.c.}}{\text{Equivalent weight of acid}}.$$

Any five of the above factors being known, the sixth can be determined.

N.B.—Do not try to remember too many formulæ. Try to argue out your results as explained above, and then you will not find yourself in difficulties if you forget the formula.

The above result may be obtained by working out the calculation in terms of normality.

Data :—

Strength of sodium hydrate solution=0·0038 gram per c.c.

A normal sodium hydrate solution contains 0·04 gram NaOH per c.c.

$\therefore$ Normality of solution $= \frac{0{\cdot}0038}{0{\cdot}040} = 0{\cdot}095\,N.$

By experiment 25 c.c. of 0·095 N sodium hydrate are neutralised by 19 c.c. of hydrochloric acid.

∴ Strength of hydrochloric acid is $\frac{25}{19} \times 0{\cdot}095\,N = 0{\cdot}125\,N$.

But a normal solution of hydrochloric acid contains 0·0365 gram hydrochloric acid per c.c.

∴ A 0·125 N solution of hydrochloric acid contains
(0·0365 × 0·125) gram hydrochloric acid per c.c.
=0·00456 *gram hydrochloric acid per c.c.* . . . *Ans.*

DEMONSTRATION 48

EXPT. 216.—(*a*) **To prepare a decinormal solution of sodium carbonate.** (*b*) **To standardise a given solution of nitric acid.**—(*a*) The molecular weight of sodium carbonate, Na_2CO_3, is $2 \times 23 + 12 + 16 \times 3 = 106$.

From the equation $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$ it can be seen that one molecule of sodium carbonate requires *two* equivalents of hydrochloric acid for its decomposition.

$\therefore$ The equivalent weight of sodium carbonate is $\frac{106}{2} = 53$.

It is required to make a decinormal solution of sodium carbonate, *i.e.*, a solution containing 5·3 grams of sodium carbonate in one litre of solution. (See page 226.)

Take either some chemically pure sodium carbonate or sodium bicarbonate and powder it finely in a mortar. Heat it strongly in a crucible until its weight is constant. Allow the vessel to cool in a desiccator each time. (Do not put the vessel in the desiccator until it has cooled sufficiently for you to be able to bear your hand close to it.)

In the case of sodium carbonate any water present is driven off and the salt is left anhydrous.

In the case of sodium bicarbonate the following action takes place:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

and anhydrous sodium carbonate is left behind.

Weigh a small stoppered glass weighing bottle very carefully and note the weight *in your note-book at once.*

Weigh out 2·65 grams of your pure dry powdered sodium carbonate in the little weighing bottle. Add or withdraw the salt by means of a clean, dry spatula.

Select a clean, dry, glass funnel and a thin glass rod which will just pass through the stem of the funnel. Place the funnel in the neck of a clean 500 c.c. flask *into which a little distilled water has been poured.* Spill the dry sodium carbonate from the weighing bottle into the funnel and help the powder through the neck by means of the glass rod. Do not let the glass rod slip through the funnel or it will make a hole in your flask. *When* all the powder has been added and only traces cling to the walls of the funnel and to the bottle and rod, wash all these instruments thoroughly with distilled water and pour the washings through funnel into the flask.

NOTE.—Do not attempt to shift a block in the neck of the funnel by adding water. If you do so the sodium carbonate combines with water and, in doing so, swells and makes the obstruction harder than before. If your carbonate is properly powdered any stoppage can always be removed by shaking or by gentle pressure with the glass rod. Give the rod a twisting motion as you press the obstruction.

2. Water is put in the flask to a depth of about 0·25 inch to prevent the sodium carbonate forming a cake on the bottom of the flask. This would happen if all the carbonate were added first and then water poured on top of it. The error is not irremediable as the caked sodium carbonate will dissolve eventually, but it results in loss of time.

Add sufficient cold, distilled water to make the solution up to 500 c.c., and shake up the solution thoroughly.

This will be a decinormal solution and contains 0·0053 gram of sodium carbonate per c.c.

(*b*) **To standardise (estimate the strength of) the nitric acid supplied.**—Wash your burette first with water, then with the given nitric acid solution. Clamp the burette in the stand. Pour nitric acid into the burette by means of a funnel and see that there are no bubbles in the tap.

Read again all the instructions given in the previous demonstration.

Use 20 or 25 c.c. of sodium carbonate for each titration. Use a teacup.

Use methyl-orange as indicator.

From the equation

$$\begin{array}{l} Na_2CO_3 + 2HNO_3 = 2NaNO_3 + H_2O + CO_2 \\ \quad 106 \quad + 2 \times 63 \end{array}$$

we see that 53 grams of sodium carbonate are equivalent to 63 grams of nitric acid.

Write out your data and calculate the strength of the nitric acid solution in a similar manner to that shown in the previous demonstration.

(*c*) Litmus is not reliable as an indicator in the presence of carbon dioxide. If, however, the solution be heated to expel the carbon dioxide then litmus may be used as an indicator for the titration of carbonates with strong acids.

Repeat the above experiment (*b*), using litmus as indicator and an evaporating basin as the reaction vessel.

If you use a beaker or flask as reaction vessel, place a white tile or a piece of white paper under the vessel when adding acid from the burette. It facilitates the observation of any colour change.

The pink colour indicating the end-point should persist after heating.

You should get results identical with those obtained with methyl-orange as indicator.

NOTE ON THE USE OF LITMUS WITH CARBONATES.—Students frequently complain that it is difficult to obtain consistent or reliable results with litmus in carbonate determinations as litmus often seems to coagulate when the solution containing it is boiled. There is no doubt that this complaint is often justified either from the method of the preparation of the litmus solution or from some other cause.

The following method gives satisfactory results. Obtain a rough titration so that you know to 1 c.c. how much acid to add for a titration. Take your carbonate solution, add to it what you *know* will be about 1 c.c. *too little* acid. Boil the solution till the CO_2 is evolved. Now add indicator (litmus) and it will be found that the titration can be completed without coagulation taking place. It appears that *repeated* heating produces the coagulation.

DEMONSTRATION 49

EXPT. 217.—**Given a standard solution of potassium hydrate, to find the strength of a solution of potassium carbonate.**—Take the dilute sulphuric acid off your bench and dilute it with distilled water until it requires roughly 10 c.c. of the acid to neutralise 10 c.c. of one of the alkali solutions.

(The dilute sulphuric acid is not of constant strength in all laboratories, but try adding about 9 c.c. of the bench dilute sulphuric acid to 500 c.c. of distilled water. *Shake up well to ensure thorough mixing.*)

Wash out your burette, first with distilled water and then with the dilute acid you have just made up. Observe the precautions given in the previous exercises.

Fill your burette with the acid.

Now titrate 25 c.c. of each of the given solutions (potassium carbonate and potassium hydrate) against the dilute sulphuric acid.

Use methyl-orange as indicator.

Write down your titrations *at once* in your note-book.

Suppose as a result of your experiments you find that x c.c. of acid neutralise 25 c.c. of KOH solution, and y c.c. of acid neutralise 25 c.c. of K_2CO_3 solution.
Then

$$1 \text{ c.c. of acid neutralises } \frac{25}{x} \text{ c.c. of KOH solution,}$$

and $$1 \text{ c.c. of acid neutralises } \frac{25}{y} \text{ c.c. of } K_2CO_3 \text{ solution.}$$

In other words $\frac{25}{x}$ c.c. of KOH contain as much base as $\frac{25}{y}$ c.c. of

K_2CO_3 because they are capable of neutralising the same quantity of acid (*i.e.* the amount of acid in 1 c.c. of solution).

Suppose the strength of the KOH is S grams KOH per c.c.

Weight of KOH in $\frac{25}{x}$ c.c. $= \frac{25S}{x}$ grams.

But, since the equivalent of KOH is 56 and the equivalent of potassium carbonate, K_2CO_3, is $\left(\frac{78+12+48}{2}\right) = \frac{138}{2} = 69$.

$\therefore \left(\frac{25 \times S}{x}\right)$ grams of KOH are equivalent to $\left(\frac{25}{x} \times S \times \frac{69}{56}\right)$ grams of K_2CO_3.

But this is the weight of K_2CO_3 in $\frac{25}{y}$ c.c.

$\therefore$ Weight of K_2CO_3 in 1 c.c. of solution $= \left(\frac{25}{x} \times S \times \frac{69}{56} \times \frac{y}{25}\right)$ grams

$$= \left(\frac{y}{x} \times S \times \frac{69}{56}\right) \text{ grams } K_2CO_3.$$

y and x have been determined by experiment. S is known. (You do not need to know the strength of the acid solution used.)

$\therefore$ *Required strength of potassium carbonate is. . . grams per c.c. Ans.*

NOTE.—Solutions of bicarbonates are titrated in exactly the same way as carbonates, using litmus or methyl-orange as indicator.

DEMONSTRATION 50

EXPT. 218.—**To make a decinormal solution of sulphuric acid from the acid on your bench.**—Take some of the dilute sulphuric acid from your bench, dilute it about 40 times with distilled water and *thoroughly mix the solution by shaking it.* Or, take strong sulphuric acid from your bench and dilute it about 200 times with distilled water, adding the acid cautiously to the water. *Shake to mix thoroughly.*

Wash out the burette with distilled water and then with the dilute acid. Then fill the burette with the acid and titrate the acid against a standard alkali.

Then

$$\frac{\text{number of c.c. of alkali} \times \text{strength of alkali in grams per c.c.}}{\text{equivalent weight of alkali}}$$

$$= \frac{\text{number of c.c. of acid} \times \text{strength of acid in grams per c.c.}}{\text{equivalent weight of acid}}.$$

From this the strength of the acid is obtained in grams per c.c.

Let it be x gram H_2SO_4 per c.c.

To take the particular example in question, sulphuric acid $H_2SO_4 = 2 + 32 + 64 = 98$ is a dibasic acid and its equivalent weight is 49.

A decinormal solution contains 4·9 grams H_2SO_4 per litre, *i.e.*, 0·0049 gram H_2SO_4 per c.c.

If the strength of the acid, as determined by the above experiment and calculation, works out at less than 0·0049 gram H_2SO_4 per c.c., *the experiment must be started again, using acid which has been less diluted.* The degree of dilution can readily be found by simple calculation.

Suppose the calculated strength x grams H_2SO_4 per c.c. is greater than 0·0049, then, by adding water to the standardised acid, the strength can be reduced to 0·0049 gram per c.c.

To find the amount of water to be added to v c.c. of standardised acid :—

Weight of the acid in v c.c. $= v \times x$ grams H_2SO_4.

$\therefore$ If the strength is to be 0·0049 gram H_2SO_4 per c.c. the volume of the acid will be $\left(\frac{v \times x}{0{\cdot}0049}\right)$ c.c. Mix thoroughly.

Take v c.c. of your acid and add sufficient distilled water from a burette to make the volume up to $\left(\frac{v \times x}{0{\cdot}0049}\right)$ c.c. Mix thoroughly.

Conversely, to have just one litre of $N/10$ acid we must take $\left(1000 \times \frac{0{\cdot}0049}{x}\right)$ c.c. of the standardised acid and make that volume up to one litre. Mix thoroughly by shaking.

Note.—By " making the volume up " to a given volume any error due to the contraction of the solution on dilution is avoided. This error is negligible in such weak solutions as are being used here.

DEMONSTRATION 51

EXPT. 219.—**Estimation of the percentage of ammonia in an ammonium salt.**—Fit up an apparatus as shown in Fig. 71, and see that all fittings are air-tight. Round off the ends of all tubes before pushing them through the corks.

Notice that the tube directly connected to the side-tube of the distillation flask does not reach the bottom of the flask into which it dips. This is to prevent liquid from getting sucked into the distillation flask.

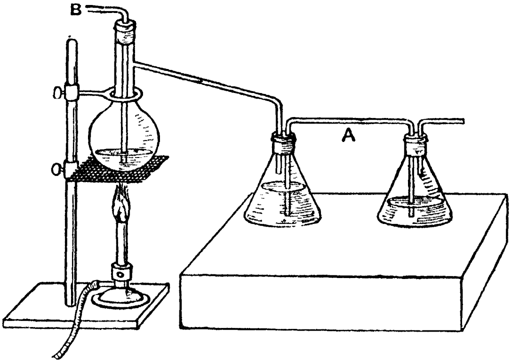


FIG. 71.

The tube *A* dips to the bottom of both flasks. The first should be of about 500 c.c. capacity, and the second about 300 c.c. capacity.

Finely powder some ferrous ammonium sulphate crystals and put about 2·5 grams into a weighing bottle. Weigh the salt and the bottle accurately. Shoot the salt into the distillation flask by means of a glass funnel, taking care to hold the flask in such a position that none of the salt goes down the side-tube. Now weigh the weighing bottle again.

The difference in these two weighings gives the weight of the salt taken.

Let it be denoted by w.

Add some water to dissolve the salt, also some glass beads.

Into the 500 c.c. flask put 350 c.c. of standard acid of about $N/10$ strength, and into the 300 c.c. flask put 50 c.c. of the same acid. Then total volume of standard acid used = 400 c.c.

Fit the apparatus together. Now pour some strong caustic soda solution into the distillation flask and replace the cork containing the long tube shown in the figure.

When the caustic soda is added a dirty green precipitate forms. It is for this reason that the salt is dissolved before adding caustic soda. If the caustic soda were added to the solid salt it would form a gelatinous mass over the surface of the crystals and it would be very difficult to ensure that all the salt would be attacked. If all the products of the reaction were either volatile or soluble it would not be necessary to dissolve the original solid before adding the caustic soda, though it would not be incorrect to do so.

Boil the liquid in the distillation flask. The ammonium salt will be decomposed according to the equation

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3.$$

The ammonia gas passes along the delivery tube and, dissolving in the dilute sulphuric acid, neutralises a portion of it.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

Some steam will have been given off during the boiling, and so the volume of the sulphuric acid will have increased a little. Blow air through the side tube B to drive out the last traces of ammonia.

Make it up to some known volume, say 450 c.c. Take 50 c.c. for each titration and standardise against standard caustic soda solution, using litmus or methyl-orange as indicator.

Strength of caustic soda $= y$ grams per c.c.
Quantity of caustic soda required for each titration $= v$ c.c.

Total quantity of soda used for neutralisation of the acid not neutralised by the ammonia

$$= v \times \frac{450}{50} = 9v \text{ c.c.}$$
$$= 9vy \text{ grams NaOH.}$$

This is equivalent to $9vy \times \frac{49}{40}$ grams H_2SO_4.

Suppose the strength of the sulphuric acid used was z grams per c.c.,
then weight of sulphuric acid used $= 400z$ grams,
and weight of sulphuric acid used to neutralise the ammonia
$= \left\{400z - \left(\frac{49}{40} \times 9vy\right)\right\}$ grams H_2SO_4.

But 49 grams of sulphuric acid are equivalent to 17 grams of ammonia,
∴ the weight of ammonia neutralised was

$$\frac{17}{49}\left\{400z - \left(\frac{49}{40} \times 9vy\right)\right\} \text{ grams } NH_3.$$
$$= x \text{ grams ammonia (suppose).}$$

Weight of salt taken $=$ w grams.
Weight of ammonia in w grams of salt $=$ x „
Weight of ammonia in 1 gram of salt $=$ $\frac{x}{w}$ „
Weight of ammonia in 100 grams of salt $=$ $\frac{x}{w} \times 100$ „

Substituting for x we have :
Percentage of ammonia in the given salt is

$$\frac{17}{49} \times \frac{100}{w}\left\{400z - \left(\frac{49}{40} \times 9vy\right)\right\}.$$

∴ *Required percentage of ammonia = . . . % Answer.*

A simpler apparatus may be employed—(see Figs. 72 and 73).

Instead of the pipette and flask containing acid a funnel and a beaker may be used for the absorption apparatus.

The above is a general method applicable to *all* ammonium salts, but if all the products of reaction are soluble or volatile the following procedure is also applicable.

e.g., Suppose you are required to find the percentage of ammonia in commercial ammonium salt.

Boil a weighed quantity of the ammonium salt with a known volume of standard caustic soda. After all the ammonia is expelled (use turmeric paper to test for the gas) make up the volume of the solution to the original volume. (Some water will be lost as steam.) Titrate the excess of soda against a standard acid solution and calculate the result in a manner similar to that explained in the above experiment.

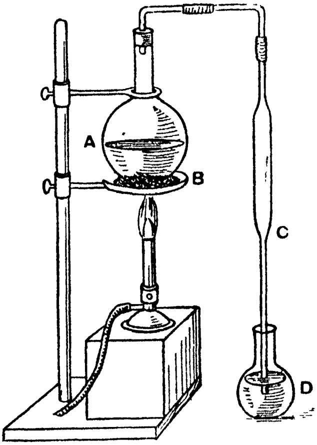


Fig 72

A, Ammonium salt, water and caustic soda.
B, Sand-bath.
C, 25 c c. pipette.
D, Flask containing standard acid. Pipette tube dips about ½ inch below surface of acid.

Instead of a pipette and flask containing standard acid, the acid may be put in a beaker and the ammonia passed in by means of an inverted funnel.

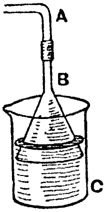


Fig. 73.

A, Connection to flask.
B, Funnel.
C, Beaker.

DEMONSTRATION 52

EXPT. 220.—**To estimate the amounts of sodium hydrate and sodium carbonate in a solution containing both the substances.**—You are given a standard solution of hydrochloric acid

1 c.c. $= z$ grams HCl.

This estimation depends upon the fact that the indicator phenolphthalein only shows when the acid has converted the sodium carbonate to bicarbonate, *i.e.*, the end-point of the reaction represented by the equation

$$\underset{\substack{\text{Sodium}\\ \text{carbonate}}}{Na_2CO_3} + HCl = \underset{\substack{\text{Sodium}\\ \text{bicarbonate}}}{NaHCO_3} + NaCl$$

In order to decompose the sodium carbonate completely two molecules of hydrochloric acid are required for one molecule of sodium carbonate.

When phenolphthalein is added to a solution of sodium carbonate it gives to the solution a pink colour which is destroyed when, by the addition of acid, the reaction shown in the above equation is completed.

Sodium hydrate solution also gives a pink colour to phenolphthalein, and this is also turned colourless when hydrochloric acid is added.

If therefore a measured quantity of the alkali solution is taken and phenolphthalein added we can, by running in standard hydrochloric acid, indicate the amount of acid required (*a*) to neutralise all the NaOH, plus (*b*) the amount of acid required to convert the carbonate into bicarbonate.

This will be called the " first titration."

Put the acid in the burette.

Use 25 c.c. of the given alkali solution for each titration.

Read your burette and note the reading in your note-book.

At the end of the "first titration" the solution will be colourless.

To the same solution add a little methyl-orange. The solution is yellow. Now run in acid until the solution turns pink.

Read your burette and note the reading in your note-book.

The "second titration" shows the amount of acid required to decompose the bicarbonate.

From this it will be seen that the sodium carbonate is decomposed in two stages *each of which* requires the same quantity of hydrochloric acid.

Each of these quantities is the amount represented by second titration.

Write down your titrations in tabular form. (See page 248)

Suppose the "first titration" (end-point indicated by phenolphthalein) requires x c.c. of standard acid, and that the "second titration" (end-point indicated by methyl-orange) requires y c.c. of standard acid.

Since 25 c.c. of the alkali were used for each titration,

Then quantity of acid required by the carbonate in 25 c.c. of mixture is $2y$ c.c., and quantity of acid required by the hydrate in 25 c.c. of the mixture is $(x-y)$ c.c.

But the strength of the standard acid is z grams per c.c.

∴ Quantity of carbonate in one litre of solution

$$= \left(2y \times z \times \frac{53}{36\cdot5} \times \frac{1000}{25}\right) \text{ grams } \mathrm{Na_2CO_3} \text{ per litre,}$$

and quantity of sodium hydrate in one litre of solution

$$\left\{(x-y) \times z \times \frac{40}{36\cdot5} \times \frac{1000}{25}\right\} \text{ grams } \mathrm{NaOH} \text{ per litre.}$$

$$\therefore \textit{Given solution contains} \left\{\begin{array}{l} \ldots\ \textit{grams}\ \mathrm{Na_2CO_3}\ \textit{per litre} \\ \ldots\ \textit{grams}\ \mathrm{NaOH}\ \textit{per litre} \end{array}\right\} \textit{Ans.}$$

DEMONSTRATION 53

EXPT. 221.—(*a*) **To determine the equivalent weight of an acid. (*b*) To determine the basicity of an acid of known molecular weight. (*c*) To determine the molecular weight of an acid of known basicity.**—The method of procedure in all these cases is to weigh out a quantity of the acid, make a solution of it in water and then titrate against a standard alkali.

In these experiments a strong base must be used, *e.g.*, sodium or potassium hydrate with phenolphthalein as indicator. If a strong acid were given, litmus or methyl-orange would do, but, as you do not know the nature of your acid, the indicator of the widest application must be employed, viz., phenolphthalein.

The method of finding the equivalent weight of acid will be given in detail.

Take a clean weighing bottle and put in it about 2·5 grams of the acid. Transfer the acid to a 250 c.c. flask by means of a glass funnel. Weigh the weighing bottle and the residue of acid. The acid left sticking to the funnel is washed into the flask and water added to make up the total volume of the acid to 250 c.c. Shake up thoroughly to ensure complete mixing.

Wash your burette first with distilled water and then with your acid solution. Fill the burette with the acid.

Take 20 c.c. of the caustic soda supplied for each titration. The caustic soda is of approximately $N/10$ strength.

Repeat your titrations until constant results are obtained.

Write down your weighings and other observations *at once in your note-book.*

Enter your results thus :—

Weight of weighing bottle and acid $= W$ grams.
Weight of weighing bottle and residue $= w$ „
∴ Weight of acid taken $= (W-w)$ „

The acid was dissolved in distilled water and the solution made up to 250 c.c.

Strength of the acid is $\left(\frac{W-w}{250}\right)$ grams per c.c.

Strength of caustic soda solution $= a$ grams NaOH per c.c.

Volume of caustic soda used for each titration $=$ 20 c.c.

Indicator—phenolphthalein.

Titrations :—

Height of burette at beginning	...c.c.	...c.c.	...c.c.	...c.c.	...c.c.
Height of burette at end ..	...c.c.	...c.c.	...c.c.	...c.c.	...c.c.
Volume run in	...c.c.	...c.c.	...c.c.	...c.c.	...c.c

Average $= x$ c.c. of acid.

By definition :—

The equivalent weight of the acid is the number of grams of the acid which are required to neutralise one gram equivalent (*i.e.*, 40 grams) of caustic soda.

From the above data :—

Number of grams of acid required to neutralise $20a$ grams of

$$\text{NaOH} = \frac{x(W-w)}{250}.$$

Number of grams of acid required to neutralise 1 gram of

$$\text{NaOH} = \frac{x(W-w)}{20a \times 250}.$$

Number of grams of acid required to neutralise 40 grams of

$$\text{NaOH} = \frac{40x(W-w)}{20a \times 250} = \frac{x(W-w)}{125a}.$$

∴ *Required equivalent weight of given acid* $=$ . . . *Ans.*

(*b*) If you are given the molecular weight of the acid find the equivalent weight as described above and the basicity is determined from the ratio

$$\frac{\text{molecular weight of acid}}{\text{equivalent weight of acid}} = \text{basicity}.$$

(*c*) Given the basicity, to find the molecular weight.

Find the equivalent weight of the acid in the manner described above.

Then

basicity × equivalent weight of acid $=$ molecular weight of acid.

DEMONSTRATION 54

EXPT. 222.—**To estimate the strength of a given solution of calcium chloride.**—When sodium carbonate solution is added in excess to a solution of calcium chloride all the calcium present will be precipitated as calcium carbonate. (*Cf.* Expt. 87, page 93.)

$$\underset{\underbrace{40+35{\cdot}5\times 2}_{111}}{\mathrm{CaCl_2}} + \mathrm{Na_2CO_3} = \mathrm{2NaCl} + \underset{\underbrace{40+12+48}_{100}}{\mathrm{CaCO_3}}$$

From this equation we see that 111 grams of calcium chloride are equivalent to 100 grams of calcium carbonate.

When calcium carbonate is dissolved in hydrochloric acid the equation

$$\underbrace{\mathrm{CaCO_3}}_{100} + \underbrace{\mathrm{2HCl}}_{73} = \underbrace{\mathrm{CaCl_2}}_{111} + \mathrm{H_2O} + \mathrm{CO_2}$$

shows that 100 grams of calcium carbonate are equivalent to 73 grams of hydrochloric acid.

∴ 73 grams of hydrochloric acid are equivalent to 111 grams of calcium chloride.

By determining how much hydrochloric acid is required to dissolve the calcium carbonate produced from given volume of calcium chloride solution, the weight of calcium chloride can be determined $\left(\text{multiply the weight of hydrochloric acid by } \frac{111}{73}\right)$.

The procedure is as follows :—

An excess of sodium carbonate solution is added to a known volume of given solution of calcium chloride. The calcium is quantitatively precipitated as calcium carbonate and the amount of hydrochloric acid required to dissolve that carbonate is estimated.

In practice the precipitate of calcium carbonate is dissolved in excess of standard acid and the excess of standard acid is determined by a solution of sodium carbonate of known strength.

Take x c.c. of given calcium chloride solution, and to it add sodium carbonate solution. Shake or stir thoroughly.

Filter off the precipitate of calcium carbonate.

The precipitate of calcium carbonate is washed with distilled water until the washings show no signs of alkalinity.

Now dissolve the precipitate of calcium carbonate by pouring over it a known volume (v c.c.) of standard hydrochloric acid, and wash the filter paper by pouring over it distilled water. Mix the washings with the original solution and make up to a known volume ($2v$ c.c.). See that you have completely dissolved the precipitate and that the solution is distinctly acid.

Put some of this solution in a burette and titrate it against a standard solution of caustic soda.

Use methyl-orange as indicator.

Write down your data clearly.

Volume of given solution of calcium chloride taken = x c.c.
Volume of hydrochloric acid taken to dissolve the precipitate = v c.c.
This volume, after adding washings, became = $2v$ c.c.
Strength of the acid = a grams HCl per c.c.
Volume of caustic soda used for each titration = 10 c.c.
Strength of caustic soda used = b grams NaOH per c.c.
Indicator, methyl-orange.

Titrations :—

Height of burette at beginning	...c.c.	...c c.	...c.c.	...c.c.	...c.c.
Ditto at end	...c.c.	...c.c.	...c.c	...c c.	...c.c.
Volume run in	...c c.	...c c	.. c c.	...c c.	...c.c.

Average quantity of acid used y c.c. for 10 c.c. of soda.

Total quantity of soda required $= \left(\frac{2v\times 10}{y}\right)$ c.c.

Weight of NaOH in this is $\left(\frac{2v\times 10}{y}\right)\times b$ grams NaOH.

This is equivalent to $\frac{2v}{y}\times 10\times b\times\frac{36{\cdot}5}{40}$ grams HCl

$=\frac{36{\cdot}5bv}{2y}$ grams HCl.

Total quantity of HCl used $=(v\times a)$ grams HCl.

Quantity of HCl required to dissolve the calcium carbonate

$$=\left(va-\frac{36{\cdot}5bv}{2y}\right)\text{ grams HCl.}$$

Now from the equation

$$\underset{100}{\underbrace{\underset{(40+12+48)}{CaCO_3}}} + \underset{73}{\underbrace{\underset{(2\times 36{\cdot}5)}{2HCl}}} = \underset{111}{\underbrace{\underset{40+2\times 35{\cdot}5}{CaCl_2}}} + CO_2 + H_2O$$

we see that

$$\left.\begin{array}{l}\text{100 grams of calcium carbonate}\\ \text{111 grams of calcium chloride}\\ \text{73 grams of hydrochloric acid}\end{array}\right\}\text{ are interequivalent.}$$

∴ $\left(va-\frac{36{\cdot}5bv}{2y}\right)$ grams of hydrochloric acid are equivalent to $\frac{111v}{73}\times\left(a-\frac{36{\cdot}5b}{2y}\right)$ grams of calcium chloride.

But this is the weight of calcium chloride in x c.c. of the solution.

∴ Number of grams of calcium chloride in one litre of the given solution is

$$\frac{111v}{73x}\left(a-\frac{36{\cdot}5b}{2y}\right)\times 1000\text{ grams.}$$

Required result:—

The solution contains . . . grams $CaCl_2$ *per litre.* *Ans.*

To calculate the result in terms of "normalities":—.

Normality of the hydrochloric acid solution = number of gram-equivalents of hydrochloric acid in one litre of solution

$$=\frac{\text{strength of hydrochloric acid}}{0{\cdot}0365}=\frac{a}{0{\cdot}0365}=n\text{ (suppose).}$$

When diluted from volume v_0 to v_1 normality will become

$$n\times\frac{v_0}{v_1}=n_0\text{ (suppose).}$$

But let the normality actually found after the acid has dissolved the $CaCO_3=n_1$.

Then number of equivalents used up in dissolving the

$$CaCO_3=(n_0-n_1).$$

But the gram-equivalent weight of $CaCl_2=\frac{111}{2}=55{\cdot}5$.

∴ $(n_0-n_1)\times 55{\cdot}5$ = *number of grams of* $CaCl_2$ *dissolved in one litre of solution. . . . Ans.*

Note to Demonstrators

Suitable quantities for the performance of this experiment are as follows :—

Make a solution of calcium chloride by dissolving about 2·5 grams of pure calcium carbonate in dilute hydrochloric acid and make it up to 100 c.c.

This will enable you to check the accuracy of the final results.

Take 25 c.c. of this solution and add the sodium carbonate solution to it. This had better be done in a flask or in a beaker covered with a watch glass, otherwise the effervescence (due to the action of sodium carbonate on the excess of the acid used in dissolving calcium carbonate) may cause a certain amount of loss.

Filter, wash and use 250 c.c. of approximately $N/10$ hydrochloric acid to dissolve the precipitate.

Make the filtrate and washings up to 500 c.c.

Use approximately $N/20$ sodium hydrate for the titrations

DEMONSTRATION 55

PRECIPITATION METHOD No. 2

EXPT. 223.—**Estimation of the percentage of barium in a given solution of a barium salt.**—In this case a known volume of the solution of the barium salt is precipitated by a *standard* solution of sodium carbonate. The precipitate of barium carbonate is filtered off and the filtrate, after being made up to a known volume, is titrated against a standard acid.

In this manner one estimates the amount of carbonate which has been used up in precipitating the barium according to the equation

$$\underset{(137+2x)}{BaX'_2} + \underset{106}{Na_2CO_3} = BaCO_3 + 2NaX'$$

Multiply the mass of sodium carbonate used up by $\frac{137}{106}$ and you obtain the weight of barium which was precipitated by it.

The method is the same as that described in the following problem:—

EXPT. 224.—**Determine the number of molecules of water of crystallisation in the given crystals of barium chloride.**—Weigh out a known amount of barium chloride, keeping in mind the fact that the equivalent weight of barium chloride is at least 104 $\left(i.e., \frac{137+2\times35\cdot5}{2}\right)$.

Take 2·5 to 3 grams of barium chloride and dissolve them in water (100 c.c.).

The solution so produced will be somewhat less than $N/10$. To this solution add 100 c.c. of $N/2$ sodium carbonate.

Filter off the precipitate and wash thoroughly with distilled water, adding all the washings to the filtrate. Make up washings and the filtrate to 500 c.c.

Put $N/10$ hydrochloric acid in your burette and use 25 c.c. of your solution of carbonate for each titration.

Use methyl-orange as indicator.

The quantity of acid required for neutralisation of 25 c.c. will be about 20 c.c., but the exact quantity depends entirely on the quantity of barium chloride used. Suppose the volume of acid used for each titration is *a* c.c.

Data :—

Weight of weighing bottle and $BaCl_2,xH_2O$ = W grams.
Weight of weighing bottle and residue = w „
Weight of $BaCl_2,xH_2O$ taken = $(W-w)$ „
Strength of sodium carbonate solution = $N/2$ = 0·0265 gram Na_2CO_3 per c.c.
Volume of $N/2$ Na_2CO_3 solution used = 100 c.c.
Weight of sodium carbonate used = (0·0265 × 100) grams Na_2CO_3.
= 2·65 grams Na_2CO_3.
Total volume of filtrate = 500 c.c.
Volume used for each titration = 25 c.c.
Indicator, methyl-orange.
Here write the actual titrations.
Volume of $N/10$ acid required for each titration = a c.c.

Total quantity of acid required $= a \times \frac{500}{25} = 20\,a$ c.c.

Quantity of sodium carbonate represented by $(20\,a)$ c.c. of $N/10$ acid $= 20a \times 0{\cdot}0053$ grams Na_2CO_3.

Quantity of Na_2CO_3 used for the precipitation of the barium $= (2{\cdot}65 - 20 \times 0{\cdot}0053 \times a)$ grams Na_2CO_3.

But 208·4 grams of $BaCl_2$ are equivalent to 106 grams of sodium carbonate.

∴ Weight of barium chloride (anhydrous) is

$$(2{\cdot}65 - 20 \times 0{\cdot}0053 \times a)\,\frac{208}{106} \text{ grams} = W_1 \text{ grams (suppose).}$$

Now weight of salt taken was $(W-w)$ grams.

Hence we have the relationship

$$\frac{BaCl_2,xH_2O}{BaCl_2} = \frac{(W-w)}{W_1} = \frac{137+71+x\times 18}{137+71}$$

$$\text{or } \frac{W-w}{W_1} = \frac{18x+208}{208}$$

$$\text{or } x = \frac{208(W-w-W_1)}{18\,W_1}$$

All these quantities are known except x.

∴ *Required number of molecules of water of crystallisation is . . . Ans.*

DEMONSTRATION 56

EXPT. 225.—**Estimation of a solution of sodium chloride by silver nitrate solution of known strength.**—When silver nitrate is added to a solution of sodium chloride the reaction which takes place is quantitative and is represented by the equation

$$\underset{\underbrace{23+35{\cdot}5}_{58{\cdot}5}}{\mathrm{NaCl}} \quad + \quad \underset{\underbrace{108+14+48}_{170}}{\mathrm{AgNO_3}} \quad = \quad \mathrm{AgCl}+\mathrm{NaNO_3}$$

The silver chloride forms an insoluble precipitate and is thus removed from the sphere of action. A normal solution of silver nitrate contains 170 grams of $\mathrm{AgNO_3}$ in one litre of solution.

A decinormal solution of $\mathrm{AgNO_3}$ contains 0·017 gram $\mathrm{AgNO_3}$ per c.c., or 0·0108 gram of Ag per c.c. Also—

A decinormal solution of NaCl contains 0·00585 gram NaCl per c.c., or 0·00355 gram chlorine per c.c.

The sodium chloride is measured into the "reaction vessel," and the silver nitrate solution is run in from a burette.

As soon as all the chlorine is precipitated as silver chloride there will be a slight excess of silver nitrate.

This "end-point" is shown by the indicator potassium chromate, with which silver nitrate gives a red colour, due to the formation of silver chromate.

$$2\mathrm{AgNO_3} \quad + \quad \mathrm{K_2CrO_4} \quad = \quad \underset{\substack{\text{Red precipitate}\\ \text{or coloration}}}{\mathrm{Ag_2CrO_4}} \quad + \quad 2\mathrm{KNO_3}$$

This reaction, however, does not take place until the reaction between the nitrate and any soluble chloride present is completed.

In order for the estimation to be successfully carried out the *solutions employed must be neutral.*

The pink colour indicating that the reaction is completed should persist after stirring. Remember that you have a precipitate in your reaction mixture. So it is most important thoroughly to stir the solution, but *do not splash.*

Make up a standard solution of silver nitrate by weighing out 4 to 4·5 grams of pure powdered silver nitrate in a weighing bottle.

Transfer the salt to a graduated 250 c.c. flask by means of a glass funnel. Thoroughly wash all the traces of silver nitrate from the weighing bottle and the funnel and add them to the contents of the 250 c.c. flask. Make the solution up to 250 c.c.

Use only distilled water.

Make sure that your solution is thoroughly mixed. Run in the silver nitrate from the burette.

Estimate the strength of the given solution of sodium chloride.

Suppose that for 20 c.c. of your sodium chloride solution you require v c.c. of silver nitrate solution.

Strength of the silver nitrate solution $= s$ grams $AgNO_3$ per c.c.

Weight of sodium chloride equivalent to 170 grams $AgNO_3$ $= 58·5$ grams NaCl.

Weight of sodium chloride equivalent to 1 gram $AgNO_3$ $= \frac{58·5}{170}$ grams NaCl.

Weight of sodium chloride equivalent to (vs) grams $AgNO_3$ $= \left(\frac{58·5}{170} \times vs\right)$ grams NaCl.

But this is the quantity of sodium chloride in 20 c.c. of solution.

$\therefore$ *Required strength of sodium chloride solution is*

$$\frac{1}{20}\left(\frac{58·5}{170} \times vs\right) \textit{ grams } \text{NaCl} \textit{ per c.c.} \ldots \textit{Ans.}$$

DEMONSTRATION 57

EXPT. 226.—I. **Find the percentage of potassium in the given crystals of potassium chloride.**—Powder the salt.

Weigh out about 1·8 grams of it and dissolve it in water.

Make up to 250 c.c. with distilled water.

Be sure the solution is thoroughly mixed.

Use neutral potassium chromate as indicator.

Run in the standard silver nitrate from the burette.

170 grams of $AgNO_3$ are equivalent to 39 grams of potassium (as KCl).

Work out your result in a manner similar to that explained in detail in the previous demonstration.

Express your result thus :—

Required percentage of potassium in potassium chloride is . . .Ans.

II. **Find the amount of chlorine present as chlorides in tap-water.**—Use $N/100$ $AgNO_3$. See that all the solutions used are neutral. Express your result as parts per million.

NOTE.—Always keep your silver nitrate solutions in brown bottles.

Oxidation by Potassium Permanganate.

Potassium permanganate solution may be used in the presence of sulphuric acid as an oxidising agent.

Its formula may be taken as $K_2Mn_2O_8$ and, as it crystallises without water of crystallisation, its molecular weight is $2 \times 39 + 2 \times 55 + 8 \times 16 = 316$.

To find out what is the equivalent weight of the substance when it is used as an oxidising agent we must see how much oxygen, capable of being used for purposes of oxidation, it contains in one gram-molecule.

With sulphuric acid in dilute aqueous solution the action in the presence of an oxidisable substance is

$$\underset{316}{K_2Mn_2O_8} + 3H_2SO_4 = 3H_2O + K_2SO_4 + 2MnSO_4 + \underset{80}{5O}$$

i.e., 316 grams of potassium permanganate contain 80 grams of oxygen which are capable of being used as an oxidising agent.

Such oxygen is called "available oxygen."

Now a normal solution of an oxidising agent is a solution which contains in one litre 8 grams of "available oxygen," *i.e.*, the number of grams of oxygen which would convert one gram of hydrogen into water.

316 grams of potassium permanganate contain 80 grams of "available oxygen."

Therefore the normal solution of potassium permanganate contains 31·6 grams of $K_2Mn_2O_8$ per litre.

There are three ways of expressing the strength of a potassium permanganate solution.

(1) The number of grams of potassium permanganate per c.c.

(2) The number of grams of "available oxygen" per c.c.

(3) The number of grams of iron which one c.c. is capable of oxidising from the ferrous to the ferric state.

From the equation

$$\underset{\substack{\text{Ferrous oxide}\\ 2\times 56}}{2FeO} \quad + \quad \underset{\substack{\text{Oxygen}\\ 16}}{O} \quad = \quad \underset{\text{Ferric oxide}}{Fe_2O_3}$$

it can be seen that 8 grams of oxygen will convert 56 grams of iron from the ferrous to the ferric state.

Therefore a normal solution of potassium permanganate may have its strength stated thus :—

1 c.c. contains 0·0316 gram of potassium permanganate.
1 c.c. contains 0·008 gram of "available oxygen."
1 c.c. is equivalent to 0·056 gram of iron.

The permanganate solution is always run in from the burette. Read the top edge of the layer of liquid. The solution is too dark to allow you to see the curve of the meniscus properly.

When potassium permanganate is run into a solution in the presence of sulphuric acid it colours the solution pink, but if an oxidisable substance is present the permanganate gives up its "available oxygen," and colourless salts of potassium and manganese are formed. Hence, so long as there is any oxidisable substance present, the potassium permanganate is decolorised as soon as it is run into the solution. When all possible oxidation has taken place, the addition of a drop of potassium permanganate in excess gives to the solution a pink coloration and indicates that the reaction is finished.

Potassium permanganate acts as its own indicator and shows the "end-point" by a permanent pink coloration.

Always use a burette with a glass tap. Rubber is likely to be attacked by the potassium permanganate.

If the solution goes brown during the addition of the potassium permanganate, it is possibly due to the fact that you have not added the sulphuric acid or that the quantity added is insufficient. Try also adding the permanganate more slowly and stirring more thoroughly in a fresh titration.

Potassium permanganate crystals are liable to be impure and the strength of the solution is liable to alter through decomposition, so it is better, for accurate work, to standardise your solution each time before use.

Keep permanganate solutions in dark-coloured bottles or in a cool, dark cupboard.

It is important that all water used should be "air-free."

DEMONSTRATION 58

EXPT. 227.—(i) **To prepare a decinormal solution of ferrous ammonium sulphate and** (ii) **from this standard solution, to prepare a** *N*/10 **solution of potassium permanganate.**—Crystals of ferrous ammonium sulphate can be obtained in a pure state, and are not likely to undergo decomposition.

The formula of the crystals is $FeSO_4,(NH_4)_2SO_4,6H_2O$.

Molecular weight $= 56 + 96 + 36 + 96 + 108 = 392$.

It is convenient to remember that ferrous ammonium sulphate contains one-seventh of its weight of iron in a molecule.

A normal solution of a ferrous salt contains as much iron as will be oxidised by 8 grams of oxygen, *i.e.*, 56 grams of iron or 392 grams of $FeSO_4,(NH_4)_2SO_4,6H_2O$.

Therefore to make a decinormal solution we must dissolve 39·2 grams of ferrous ammonium sulphate in water and make the solution up to 1000 c.c. (1 litre).

Weigh out carefully 19·6 grams of pure powdered ferrous ammonium sulphate in a weighing bottle.

Weigh the bottle first, as the last traces of salt must be washed from the bottle to the flask by air-free water. It will be found convenient to add a few drops of dilute sulphuric acid to the water used for dissolving the salt.

Make the solution up to 500 c.c. by air-free distilled water in a stoppered graduated flask.

Put in the stopper and shake the flask thoroughly.

Weigh out in a weighing bottle 1·6 to 1·7 grams of pure potassium permanganate. Transfer it to a flask and dissolve it in cold water. Make the solution up to 500 c.c. and shake up thoroughly.

Put the permanganate solution in the burette.

The reaction mixture has not to be heated, so use a tea-cup for your titrations.

Take 25 c.c. of ferrous ammonium sulphate solution for each titration.

Add about 20 c.c. of dilute sulphuric acid from your bench.

Note down the reading of the burette in your note-book.

Run in the potassium permanganate until the solution in the cup has a permanent pink coloration. Be sure you stir thoroughly.

Do not be satisfied until you obtain three concordant titrations.

Remember that if your titrations are not alike the discrepancy may be due to—

(1) Imperfect mixing when making up solution.
(2) Insufficient sulphuric acid.
(3) Dirty apparatus.
(4) Improper use of your measuring instruments.

The strength of your ferrous ammonium sulphate is equivalent to (1) 0·0056 gram of iron per c.c.
(2) 0·0008 gram of oxygen per c.c.
(3) 0·00316 gram of potassium permanganate per c.c.

Suppose, as a result of the titrations, we find that 25 c.c. of the ferrous ammonium sulphate requires 22 c.c. of the potassium permanganate solution for the complete oxidation of its iron from the ferrous to the ferric state. Then the strength of the permanganate solution can be written as containing

$\frac{25}{22} \times 0{\cdot}00316$ gram of potassium permanganate per c.c.

or $\frac{25}{22} \times 0{\cdot}0008$ gram of " available oxygen " per c.c.

or equivalent to

$\frac{25}{22} \times 0{\cdot}0056$ gram of iron per c.c.

To make a decinormal solution of potassium permanganate from this solution :—

Measure out 220 c.c. of potassium permanganate solution into a 250 c.c. flask and add air-free distilled water up to the mark on the neck of the flask. Replace the stopper and shake up thoroughly. Do not leave the solution exposed to light for a long time.

DEMONSTRATION 59

EXPT. 228.—**Standardisation of potassium permanganate by means of iron wire.**—Take a piece of thin piano wire and clean it thoroughly by rubbing it with sand- or emery-paper.

Fit a clean 250 c.c. flask with a Bunsen valve.

Fig. 74 shows the structure of the Bunsen valve. Find a piece of glass tube and a piece of glass rod both of which fit the same piece of rubber tubing.

Cut off a short length of glass tube, round off the ends, and push it through a single hole cork or rubber bung which fits the neck of your 250 c.c. flask.

Carefully cut a vertical slit about half an inch long in the rubber tubing. Fit the rubber tubing on to the glass tubing and then close its end with the glass rod; see that the edges of the glass rod are rounded off.

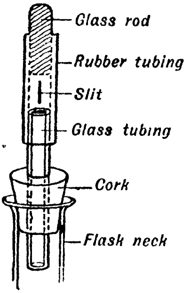


FIG. 74.

If a piece of rod of the requisite size is not available, close a piece of glass tubing and use that instead.

It will be seen that gas can come out of the flask by way of the valve, but no air from outside can enter. This prevents the liquid inside the flask from oxidation by the oxygen of the air.

Weigh out 1 to 1·5 grams of the cleaned piano wire and put it in the flask. Add dilute sulphuric acid and fit in the bung containing the Bunsen valve. Keep the flask away from naked flames. If the solution of the wire is slow, warm the flask gently by means of a water-bath.

Allow the action to continue till all the iron has dissolved, or at any rate until all action has ceased, and only minute traces of residue remain.

Cool the flask by allowing tap-water to flow over it, and then make the solution up to 250 c.c. by air-free water. Shake up thoroughly.

Put your given potassium permanganate solution into the burette.

Use 25 c.c. of the iron solution for each titration.

Do not forget to add dilute sulphuric acid.

Weight of iron taken = 1·3 grams (suppose).
∴ Strength of solution = 5·2 grams Fe″ per litre.
= 0·0052 gram Fe″ per c.c.

No. of c.c. of $K_2Mn_2O_8$ solution required to oxidise 25 c.c. of iron solution $= v$ c.c. (suppose).

Then strength of permanganate solution is equivalent to

$\left(0{\cdot}0052 \times \frac{25}{v}\right)$ gram iron per c.c.

or $\left(0{\cdot}0052 \times \frac{25}{v}\right)\frac{8}{56}$ gram "available oxygen" per c.c.

or $\left(0{\cdot}0052 \times \frac{25}{v}\right)\frac{31{\cdot}6}{56}$ gram potassium permanganate per c.c.

DEMONSTRATION 60

Expt. 229.—**To estimate the amount of iron present in a ferric salt.**—Weigh out a known amount of the salt and dissolve it in water.

The iron must now be reduced from the ferric to the ferrous state. This is done by acidifying the solution with dilute sulphuric acid and then adding zinc. The sulphuric acid forms nascent hydrogen by its action on the zinc, and the ferric iron is reduced to the ferrous state.

e.g.,

$$\underset{\substack{\text{Ferric}\\ \text{sulphate}}}{Fe_2(SO_4)_3} \underset{\text{and}}{+} \underset{\substack{\text{Nascent}\\ \text{hydrogen}}}{2H} \underset{\text{give}}{=} \underset{\substack{\text{Ferrous}\\ \text{sulphate}}}{2FeSO_4} \underset{\text{and}}{+} \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4}$$

Close your flask by means of a Bunsen valve.

DO NOT USE HYDROCHLORIC ACID

because permanganate titrations are not reliable in the presence of hydrochloric acid.

The point when all the ferric iron is reduced to the ferrous state may be determined by withdrawing a drop of the solution and bringing it into contact with a drop of potassium sulphocyanide solution on a white tile. If there is no reaction the whole of the iron has been reduced to the " ferrous " state, but if a red coloration results some ferric iron still remains.

The action must be allowed to continue until the test with potassium sulphocyanide is negative.

Withdraw solution from the flask by means of a pipette, and titrate against standard potassium permanganate solution run in from a burette. Be sure no fragments of zinc get into your "reaction vessel."

To estimate the percentage of iron in ferric alum take about 20 grams and dissolve in water. Make up to 250 c.c.

Titrate against permanganate solution which is approximately *N*/10.

DEMONSTRATION 61

EXPT. 230.—**To estimate the strength of a solution of oxalic acid by means of potassium permanganate.**—When potassium permanganate is run into an acidulated (H_2SO_4) solution of oxalic acid or an oxalate, the oxalate is oxidised.

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} + \underset{\text{on oxidation}}{O} \underset{\text{gives}}{=} \underset{\text{Water}}{H_2O} \underset{\text{and}}{+} \underset{\text{Carbon dioxide}}{2CO_2}$$

Similarly

$$\underset{\substack{\text{Ammonium}\\ \text{oxalate}}}{(NH_4)_2C_2O_4} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4} + \underset{\substack{\text{is}\\ \text{oxidised}}}{O}$$

$$\underset{\text{giving}}{=} \underset{\substack{\text{Ammonium}\\ \text{sulphate}}}{(NH_4)_2SO_4} \underset{\text{and}}{+} \underset{\text{Water}}{H_2O} \underset{\text{and}}{+} \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{2CO_2}$$

We see that 90 grams of oxalic acid are equivalent to 16 grams of oxygen.

Similarly 124 grams of ammonium oxalate are equivalent to 16 grams of oxygen.

Taking the typical case of oxalic acid, the reaction which proceeds is represented by the equation

$$\underbrace{\underset{\substack{\text{Potassium}\\ \text{permanganate}}}{K_2Mn_2O_8}}_{316} \underset{\text{and}}{+} \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{3H_2SO_4} \underset{\text{and}}{+} \underbrace{\underset{\substack{\text{Oxalic}\\ \text{acid}}}{5(COOH)_2}}_{5\times 90}$$

$$\underset{\text{give}}{=} \underset{\substack{\text{Potassium}\\ \text{sulphate}}}{K_2SO_4} \underset{\text{and}}{+} \underset{\substack{\text{Manganese}\\ \text{sulphate}}}{2MnSO_4} \underset{\text{and}}{+} \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{10CO_2} \underset{\text{and}}{+} \underset{\text{Water}}{8H_2O}$$

From this we see that 316 of potassium permanganate (*i.e.*, 80 grams of oxygen) are equivalent to $5\times 90=450$ grams of oxalic acid.

Put the standard potassium permanganate solution in the burette. Use a beaker or an evaporating basin as the " reaction vessel," because the solution has to be heated in order to make the reaction proceed to a finish.

Use 20 or 25 c.c. of oxalic acid solution for each titration. Run the oxalic acid into the beaker. Add dilute sulphuric acid. The reaction should be carried out at a temperature of about 60° C. If the beaker is just as hot as you can bear to hold with the naked hand the temperature is about right.

The end-point is indicated by the persistence of a pale pink colour in the solution.

Write your titrations in tabular form.

Suppose the strength of the potassium permanganate solution is a gram per c.c.

Volume of oxalic acid taken for each titration $=25$ c.c.

Volume of permanganate solution required for the oxidation of 25 c.c. of oxalic acid $=v$ c.c.

Let the strength of the oxalic acid solution be x gram per c.c.

$$\text{Hence } \frac{va}{25\times x}=\frac{316}{450}$$

$$\therefore\ x=\frac{450\times a\times v}{25\times 316}=\frac{9av}{158}\text{ grams per c.c.}$$

Required result $=$ . . . *grams oxalic acid per c.c.* ***Ans.***

Problems

1. Find the equivalent weight of metal of which the given substance is a pure dry basic oxide soluble in dilute hydrochloric acid.

(Given standard HCl and *N*/10 NaOH.)

2. Find the proportion in which hydrochloric and sulphuric acids are mixed in the given solution.

(You are given the total weight of acid per litre and a standard solution of a base.)

3. Find the percentage of Na_2O in a given specimen of caustic soda which has been exposed to the atmosphere. (Given standard acid.)

4. Estimate the concentration of the lime-water on your bench.

5. Find the number of molecules of water of crystallisation in the given substances.

   (*a*) Sodium carbonate.
   (*b*) Oxalic acid (two methods).
   (*c*) Ammonium chloride.
   (*d*) Ferrous sulphate.

6. The solution is a mixture of dilute nitric and hydrochloric acids. Find the percentage of each present in the solution.

7. Find the percentage of potassium carbonate and of potassium chloride present in the given commercial sample of potassium chromate.

8. Estimate the percentage of ammonia present in the commercial sample of ammonium sulphate.

9. Find the number of grams of sodium and potassium chlorides present in one litre of the given solution.

You are told the total weight of salt dissolved.

10. Estimate the percentage of sodium bicarbonate and normal carbonate in the given solution.

11. Estimate the percentage of iron present in the given sample of iron filings.

12. Find the percentage of iron in iron alum.

13. Standardise the given solution of hydrogen peroxide.

$$(5H_2O_2+3H_2SO_4+K_2Mn_2O_8=3H_2O+5O_2+K_2SO_4+2MnSO_4).$$

14. Determine the percentage of combined acid in the given commercial sample of sodium oxalate.

15. *B* is a mixture of oxalic and sulphuric acids in solution. Estimate the percentage quantity of each acid present.

16. Determine the formula of the given oxalate of iron by a volumetric method.

17. Find the equivalent weight of the given acid by a volumetric method.

18. Determine the solubility of the given oxalate at the temperature of the laboratory.

APPENDIX I

Atomic Weights

In solving problems and equations use the approximate atomic weights and valencies given in this table.

	Formula.	Atomic weight.	Valency
Aluminium	Al	27	III.
Antimony	Sb	120	“ic” V. “ous” III.
Arsenic	As	75	“ic” V. “ous” III.
Barium	Ba	137	II.
Boron	B	11	III.
Bromine	Br	80	I.
Calcium	Ca	40	II.
Carbon	C	12	IV.
Chlorine	Cl	35·5	I.
Chromium	Cr	52	VI.
Copper	Cu	63·5	“ic” II. “ous” I.
Hydrogen	H	1	I.
Iodine	I	127	I.
Iron	Fe	56	“ic” III. “ous” II.
Lead	Pb	207	II.
Magnesium	Mg	24·4	II.
Manganese	Mn	55	manganate VII. salts II.
Mercury	Hg	200	“ic” II. “ous” I.
Nitrogen	N	14	V. or III.
Oxygen	O	16	II.
Phosphorus	P	31	V. or III.
Potassium	K	39	I.
Silicon	Si	28	IV.
Silver	Ag	108	I.
Sodium	Na	23	I.
Strontium	Sr	87·6	II.
Sulphur	S	32	VI. IV. II.
Tin	Sn	118·7	“ic” IV. “ous” II.
Zinc	Zn	65·4	II.

APPENDIX II

Tension of Water Vapour (Vapour Pressure)

Temp. °C	p. (mm Hg).
0	4·57
1	4·91
2	5·27
3	5·66
4	6·07
5	6·51
6	6·97
7	7·47
8	7·99
9	8·55
10	9·14
11	9·77
12	10·43
13	11·14
14	11·88
15	12·67
16	13·51
17	14·40
18	15·33
19	16·32
20	17·36
21	18·47
22	19·63
23	20·86
24	22·15
25	23·52
26	24·96
27	26·47
28	28·07
29	29·74
30	31·51
31	33·37
32	35·32
33	37·37
34	39·52
35	41·78
36	44·16
37	46·65
38	49·26
39	52·00
40	54·87
41	57·87
42	61·02
43	64·31
44	67·76
45	71·36
46	75·13
47	79·07
48	83·19
49	87·49
50	91·98

APPENDIX III

TABLE OF LOGARITHMS.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						4	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	15	19	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	5	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	16	19	21
						2672	2695	2718	2742	2765	2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

APPENDIX III (*continued*)

TABLE OF LOGARITHMS.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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